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The Sampling and Analysis of Airborne Sulphate and Nitrates: A Review of Published Work and Synthesis of Available Information

Surveillance
Report EPS 5-AP-82-14

Air Pollution Control Directorate
March 1981

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THE SAMPLING AND ANALYSIS OF AIRBORNE SULPHATES AND NITRATES: A REVIEW OF PUBLISHED WORK AND SYNTHESIS OF AVAILABLE INFORMATION

Pollution Measurement Division
Air Pollution Control Directorate
Environmental Protection Service

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* This report was prepared for Environment Canada by Mr. R.D.S. Stevens, Concord Scientific Corporation, Downsview, Ontario, under the Department of Supply and Services Contract No. 0SS 80-00109

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Cat. No. En 42-5/82-14E
ISBN 0-662-12166-X
BEAUREGARD PRESS LIMITED

ABSTRACT

The available published information on the sampling and analytical procedures for the measurement of airborne sulphate ($SO_4^=$) and nitrate (NO_3^-) particles (droplets) was reviewed and synthesized to:

- assess the quality of existing atmospheric $SO_4^=$ and NO_3^- data;
- assess the significance of potential interferents in the Canadian setting;
- recommend alternative or modified procedures that would eliminate significant interferents;
- determine the comparability of commonly used analytical techniques for $SO_4^=$ and NO_3^- in aqueous extracts of filter-collected samples of airborne particulate matter.

Additionally, experimental data obtained by the Air Pollution Control Directorate in side-by-side sampling with different filter media during 1978 and 1979 were evaluated to determine the significance of spurious "artifact" $SO_4^=$ formation with various filter media.

The findings of this study allow an evaluation of existing $SO_4^=$ and NO_3^- data and also lead to recommended practical procedural changes that would significantly ameliorate the current unsatisfactory situation.

RÉSUMÉ

Les données publiées disponibles sur les procédés d'échantillonnage et d'analyse relativement à la mesure des particules ou gouttelettes de sulfate ($SO_4^=$) et de nitrate (NO_3^-) en suspension dans l'air ont été examinées et synthétisées afin:

- d'évaluer la qualité des données existantes sur le $SO_4^=$ et le NO_3^- atmosphériques,
- d'évaluer l'importance des interférants possibles au Canada,
- de recommander d'autres méthodes ou la modification des méthodes existantes pour éliminer les interférants importants,
- de déterminer la comparabilité des techniques analytiques les plus utilisées pour la détection du $SO_4^=$ et du NO_3^- dans les extraits aqueux des échantillons de particules de matières en suspension dans l'air recueillies sur des filtres.

De plus, les données expérimentales obtenues par la Direction générale de l'assainissement de l'air au cours d'un programme d'échantillonnage comparatif de divers milieux filtrants en 1978 et 1979 ont été evaluées afin de déterminer l'importance de la formation accidentelle "artificielle" de $SO_4^=$ avec les divers milieux filtrants.

Les résultats de cette étude permettent une évaluation des données existantes sur le $SO_4^=$ et le NO_3^- ainsi que la recommandation de changements pratiques qui amélioreraient considérablement la situation, actuellement insatisfaisante.

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ACKNOWLEDGEMENTS

The author gratefully acknowledges the generous and willing assistance and co-operation of several people in the completion of this project, and would like to thank the following in particular: Dr. B.R. Appel of the California Air and Industrial Hygiene Laboratory, Mr. Robert K. Stevens of the United States Environmental Protection Agency, Dr. C.W. Spicer of Battelle Columbus Laboratories and Dr. P.K. Mueller of the Electric Power Research Institute.

The author also wishes to express his gratitude to Carolyn Dunigan and Barbara Boyer for their competent typing and production of the report.

Finally, he wishes to express his sincere gratitude to the Government of Canada's Scientific Authority for this project, Mr. R.J. Lafleur, P.Eng., whose generous assistance, helpful advice and patience were indispensable in the completion of this report.

CONCLUSIONS

From the information reviewed and analyzed during this project, it is concluded that:

1. The atmospheric $SO_4^=$ data obtained with the widely used high volume air sampler - glass fibre filter combination are subject to a positive error which, during certain sampling periods, can be substantial. This error is due to the conversion of the SO_2 in the sampled air to $SO_4^=$ on the filter medium.
2. The magnitude of spurious $SO_4^=$ increases as air SO_2 concentration, relative humidity and filter alkalinity increase, and decreases as temperature increases. Under the more frequently encountered sampling regimes the spurious $SO_4^=$ would contribute between 1 and 3 µg $SO_4^=$ per cubic metre of air sampled, i.e. $1 \leq \Delta SO_4^= \leq 3$ µg/m^3.
3. The magnitude of the error due to spurious $SO_4^=$ formation is usually greatest in winter and least in summer. While the measured $SO_4^=$ due to spurious $SO_4^=$ formation can approach 100% in winter, it is generally less than 20% in summer.
4. The spurious $SO_4^=$ formation is induced by the filter medium and not by the co-collected particulate matter.
5. A filter's capacity to convert SO_2 to $SO_4^=$ is finite and is usually saturated after a few hours of sampling with the typical atmospheric SO_2 concentrations encountered in major urban areas. Thus, the importance of spurious $SO_4^=$ is intensified with smaller sample volumes.
6. Inert membranes, such as Teflon, or rigorously acid-washed quartz fibre or Teflon-coated glass fibre filters virtually eliminate the formation of spurious $SO_4^=$.
7. The data on airborne particulate nitrate obtained with the widely used high volume air sampler - glass fibre filter combination are in error to a variable extent, due to the occurrence of both positive and negative interferences. The magnitude of these errors could, under certain circumstances, be substantial.
8. The positive interference in the NO_3^- data (spurious or artifact NO_3^-) is caused by the adsorption of HNO_3 from the sampled air by the filter medium or, to a lesser extent, by the oxidation of airborne NO_2 to NO_3^- by the filter medium.
9. The negative interference in the NO_3^- data is caused by the reaction of co-collected H_2SO_4 with the particulate NO_3^- to release HNO_3 and/or possibly by the volatilization of some of the collected NH_4NO_3.

10. The importance of the error in the particulate NO_3^- measurement cannot be estimated reliably at this time, but, based upon the available information, it could be substantial under sampling conditions often observed in urban areas.
11. The use of inert filter media, such as Teflon, will virtually eliminate the positive NO_3^- artifact (HNO_3 adsorption and $NO_2 \rightarrow NO_3^-$ conversion), but will, if anything, increase NO_3^- losses relative to glass fibre filters.
12. No filter medium evaluated to date has a high capture-efficiency for peroxy-acetyl nitrate (PAN).
13. There is no single filter medium that can be used to determine simultaneously Total Suspended Particulate (TSP) matter and atmospheric $SO_4^=$ and NO_3^- concentrations.
14. All reported TSP data obtained with the standard high volume air sampler - glass fibre filter method are in error to some degree as a result of positive $SO_4^=$ artifact and positive and negative NO_3^- artifact formation. Because of the offsetting nature of the positive and negative interferences, and the fact that their relative significance would depend on factors related to location and time of year, it is not possible to estimate reliably the size of the error involved in the TSP determination. However, under sampling conditions likely to prevail in Canada, the error in the TSP value due to artifacts would be $\leq$ 30%.
15. For $SO_4^=$ samples obtained with glass fibre filters and high volume air samples, several analytical techniques are suitable, including the Methylthymol Blue (MTB), turbidimetric or ion chromatographic methods. For low volume samples, either the "Colovos" version of the MTB or the ion chromatographic methods would be suitable. For low volume samples obtained with membrane filters, energy dispersive X-ray analysis would also be satisfactory.
16. For NO_3^- samples obtained with the glass fibre filter - high volume air sampler combination, the automated reduction-diazotization-colorimetric (Technicon), the ion selective electrode with standard addition and the ion chromatographic methods yield virtually the same results. For low volume samples, either the ion chromatographic or the Technicon method is suitable.

RECOMMENDATIONS

As a result of the findings of this review it is recommended that:

1. The practice of the determination of airborne sulphates in Total Suspended Particulate (TSP) matter with glass fibre filters or other basic filter media be discontinued and be replaced with the use of an inert filter medium such as Teflon-coated glass fibre filters or acid-washed quartz fibre filters. Alternatively, the airborne $SO_4^=$ load could be determined using Teflon membranes in combination with low volume samplers.
2. The Teflon-coated glass fibre filter (e.g. Pallflex TX40HI20WW) be further evaluated to determine its suitability for TSP measurements. This evaluation should address such factors as:
   - the significance to the TSP determination of positive and negative NO_3^- artifacts with this filter under Canadian conditions,
   - blank values for various elements such as Pb, Fe, Na and Ca,
   - suitability for use with existing networks and protocols,
   - consistency and uniformity of product quality.
3. Depending on the results of the evaluation described in recommendation, the glass fibre filter be replaced by the Teflon-coated glass fibre filter (or a suitable alternative if this medium is found unsuitable) for TSP and $SO_4^=$ determinations.
4. An evaluation be carried out of the collection efficiency of glass fibre filters for total inorganic nitrate (gaseous and particulate) under Canadian conditions.
5. Measurements of airborne nitric acid and peroxy-acetyl nitrate be undertaken in the various regions of Canada to assess their importance to the total amount of atmospheric NO_3^- and consequently their significance to TSP determinations and to related matters (such as acid rain) in Canada.

1 INTRODUCTION

Interest in airborne sulphate particles or droplets stems primarily from the known irritant potential of sulphuric acid (H_2SO_4) and other acid sulphate species, such as ammonium bisulphate (NH_4HSO_4) (1), and the knowledge that these compounds are present in ambient air (2, 3) in varying concentrations, dependent upon location, time of year, prevailing atmospheric conditions, etc. A 1960s report (4) of airborne particulate acid concentrations in London gave typical winter and summer values of 18 $\mu g/m^3$ and 7 $\mu g/m^3$ respectively, with concentrations as high as 678 $\mu g/m^3$ reported. The evidence strongly suggested that the major acidic species was H_2SO_4. These results, along with others, led many to suspect that the principal toxin in several of the more notorious air pollution occurrences of the past (e.g. Donora, Pennsylvania, London, 1952) was airborne H_2SO_4. As a result, numerous methods to measure airborne sulphates ($SO_4^=$) have been developed, the most commonly used being the high volume air sampler - glass fibre filter combination, or "Hi Vol" method (5). Network sulphate data for certain regions of Canada (e.g. Ontario and Montreal, Quebec) using this technique are available as far back as 1969.

In addition to direct, harmful effects on human health, airborne sulphates can also play an important role in visibility reduction (6), the acidification of precipitation (7a & 7b), the global heat budget (8) and, to an unknown extent, the degradation of materials.

Recent work has also shown nitrates (NO_3^-) to be important contributors to the acidity of precipitation (7a & 7b), and since particulate NO_3^- occurs in the right size (9) to be an effective light scatterer, nitrates could, under certain conditions, also adversely affect visibility and play a role in the global heat budget. Furthermore, the recent observation of up to $\sim$ 15 ppb ($\sim$ 30 $\mu g/m^3$) of nitric acid (HNO_3) in "aged" urban air (58) raises the question of material damage and harmful effects on human health due to nitrates.

Given the increased awareness of the significance of the potential adverse effects of airborne $SO_4^=$ and NO_3^- over the past 20 years, it is not surprising that there has been a concomitant increase in the number of techniques to measure the atmospheric concentration of these two families of compounds.

By far the most widespread technique, in North America at least, has been the use of the glass fibre filter - high volume sampler combination to obtain a sample of the airborne $SO_4^=$ and NO_3^-. Part of the sample is then extracted with distilled water and analyzed for $SO_4^=$ or NO_3^- by one of several analytical techniques.

Extensive critical reviews of sampling and analytical methodologies for $SO_4^=$ have appeared previously (10, 11, 12, 13). Thus, this report will not re-discuss methods reviewed in these reports except where there are new developments or insights pertinent to these methods, shedding new light on their utility, shortcomings, or on the quality of data obtained by them.

There have been no similar comprehensive reviews for the measurement of airborne nitrates. Recently, however, several reports have appeared on work carried out to assess the suitability and/or limitations of one (or occasionally two) measurement methods for one chemical form of NO_3^- (e.g. HNO_3). The available information in this area has been reviewed and will be discussed later in this report.

The principal focus of this review will be the reported performance of various commercially available filter media in the sampling of airborne $SO_4^=$ and NO_3^- when used with a high volume air sampler (air flow $\sim$ 40 ft^3/min or $\sim$ 1.13 m^3/min), together with an evaluation of the information available on analytical methods for $SO_4^=$ and NO_3^- suitable to these filter media. Attention will also be paid to the effect of atmospheric conditions on the results obtained with these techniques.

2 SAMPLING FOR AIRBORNE SULPHATES

The use of a filter medium of some sort to collect airborne $SO_4^=$ by drawing air through the filter with a pump has been in use for at least 20 years. By far the most commonly used method is what is called the Hi Vol method. There are a number of variations of this method, but they are all essentially similar to that described in reference 14. This method offers a number of advantages, such as:

- it has excellent sensitivity (detection limit < 0.5 $\mu g/m^3$);
- sampling and analysis protocols are relatively simple;
- sampler is rugged and operational under a wide variety of weather conditions;
- sampling method allows for the determination of other constituents or parameters (e.g. TSP, Pb);
- sampling method allows the option of archiving the unused portion of the filter.

Many investigators have found this method to have drawbacks as well, including:

- conversion of some of the SO_2 in the air sample to $SO_4^=$, induced by the filter medium - this has come to be known as "spurious" or "artifact" $SO_4^=$ formation;
- failure to determine the chemical form of the $SO_4^=$; for example, H_2SO_4, $(NH_4)_2SO_4$ and $MgSO_4$ would all be determined as $SO_4^=$;
- poor time resolution, as this technique yields a 24-hour average concentration, with no diurnal variation information.

The relative seriousness of these drawbacks depends, to a large degree, upon how the data are to be used. For most applications, however, the biggest potential drawback is the formation of spurious $SO_4^=$ when the usual sampling protocol is followed, i.e. glass fibre filter and high volume air sample.

The phenomenon of spurious $SO_4^=$ formation on glass fibre filters has been recognized for about 15 years (15). Since then, many investigators have further documented the phenomenon using a number of filter media, including glass fibre. The various filters evaluated and the types of study undertaken are summarized in Table 1.

The studies have demonstrated that for basic glass fibre filters, there can be a substantial amount of SO_2 to $SO_4^=$ conversion (e.g. see references 18 and 22). For quartz fibre and more neutral filter media, the amount of spurious $SO_4^=$ formation is significantly

TABLE 1 SUMMARY OF FILTERS EVALUATED AND VARIABLES STUDIED FOR SPURIOUS $SO_4^=$ FORMATION

Variable Studied → / Filter	References: Comparative Atmospheric Sampling	SO_2 Concentration	Relative Humidity	Temperature	Sample Volume	Particulate Catalysts	O_3 Concentration	NO_2 Concentration	NH_3 Concentration	Sample Storage Conditions
Gelman AE	16,17,18,19, 20,21,23	16,17,18	16,18	16,18	16,18	16,17,18				18
Gelman Spectrograde	18,19,22,20	18,22	18,22	18,22	18,22	18,22	22	22	22	
Gelman EPA	3,18,24	18	18	18	18	18				
Gelman A	17,19,22,24, 26	17,22,26	22,26	22	22	17,22	22	22	22	
Gelman Microquartz	20	25	25							
Pallflex QAO	17,21,26	17,21,26,25	21,26,25	21,26	21	17				
Pallflex QAST	18,20	18	18	18	18	18				
Pallflex QAOS	17,26	26	26	26						
Pallflex TX40HI20WW Pallflex TX40HI20ERT	20,21,26,27	26,27	26,27	26,27	27					
Pallflex T60H20	20									
Pallflex 0X40HI	20									
Pallflex E70/2075W	18	18								
Millipore Fluoropore	17,18,22	18,22,25	22,25,22	22	22	22,28	22	22	22	
Millipore Celotate		18								
Millipore Cellulose Ester	17	17								
Millipore Mitex		18,25	25							
Millipore Duralon		18,25								
Ghia Teflo		25	25							
Ghia Zefluor		25	25							
Whatman 41	20,22,23,29, 30	22	22	22	22	22	22	22	22	
Whatmen EPM 1000	21									
ADL Microquartz	18,24	18	18	18	18	18				
MSA 1106BH	18,22	18,22	18,22	18,22	18,22	18,22	22	22	22	
MSA CT75428	16	16	16	16	16	16				
GMW-810	16	16	16	16	16					
Nuclepore	29									
BGI	12	12	12	12	12					
Delbag Polystyrene	20									
Gelman Polyimide		18								
Gelman VM-1	20									
Gelman AN 3000	20									
Gelman AN 1200	20									
Gelman AN 800	20									

reduced, and is virtually eliminated with inert membrane-type filters such as those made of polytetrafluoroethylene (e.g. "Fluoropore"). The pH and SO_2 sorption capacities of selected filter media are given in Table 2. Examination of Table 2 suggests that there is a relationship between a filter's pH and its capacity to sorb SO_2. Furthermore, other studies (16, 18, 21, 22) have revealed that other factors such as ambient SO_2 concentration, relative humidity and temperature also play a role in spurious $SO_4^=$ formation. Coutant (18) developed an empirical expression which allowed the calculation of the quantity of spurious $SO_4^=$ formation on filters as a function of ambient SO_2 concentration, relative humidity, temperature and filter alkalinity. Thus, in principle, use of this expression, given in equation 1, allows the determination of the quantity of spurious $SO_4^=$, if data on the relevant parameters are available.

TABLE 2 pH AND SO_2 SORPTION CAPACITY FOR SELECTED FILTERS*

				SO_2	
Filter Type	pH	T(°C)	RH%	Input ppb	Capacity $\mu g/cm^2$
MSA 1106BH	9.4	25	51	230	6.04
Gelman AE	9.3	25	45	236	8.03
Gelman EPA	9.3				
Pallflex QAST	8.1	14	60	286	0.27
ADL Microquartz	8.1	25	44	236	0.36
Gelman A	7.6				
Gelman Spectrograde	7.2	25	45	236	1.08
Millipore Mitex	7.2	26	50	260	0.0
Pallflex TX40HI20ERT	∿7	-	∿50	100	∿0.0
Millipore Celotate	6.7	25	65	248	0.0
Millipore Fluoropore	5.8	26	50	260	0.0
Whatman 41	4.6	-	-	-	-

* Data obtained from references 18, 22 and 27.

$$\Delta SO_4^{=} = \frac{48A}{F}\left\{0.25 + 1.57 \times 10^{-5} \exp\left(\frac{2116}{T}\right)\left(\frac{P_{SO_2}^{1/2}}{(1-RH)^{1/3}\,(1-2Z)^{1/2}}\right)\right\} \quad ...(1)$$

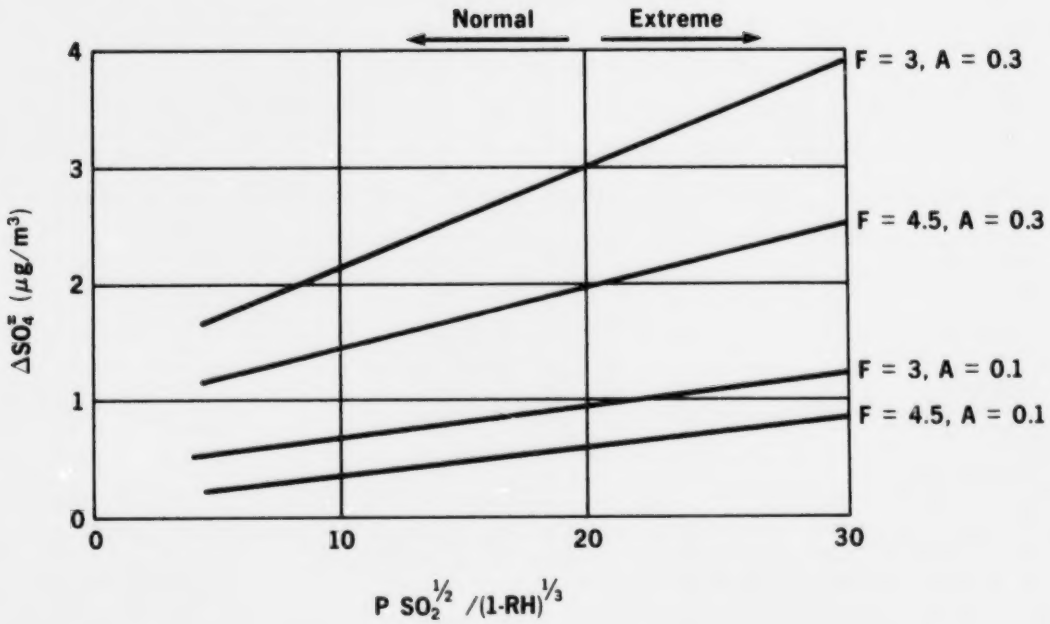
where:

$\Delta SO_4^{=}$	=	concentration of spurious sulphate ($\mu g/m^3$)
A	=	filter alkalinity (μ equivalents/cm^2)
F	=	volume of air sampled per 24-hour period per unit area (m^3/cm^2)
T	=	temperature in K°
RH	=	relative humidity
Z	=	ratio of blank $SO_4^{=}$ to metals ≈ 0
Pso_2	=	partial pressure of SO_2

Equation 1 has been found (18, 21, 22) generally to predict rather well the quantities of spurious $SO_4^{=}$ formed on fibrous filters, with differences between the quantity of predicted and observed spurious $SO_4^{=}$ usually being less than 35% of the observed value (18, 21, 22). Some of the observed differences are probably due to batch-to-batch and within-batch variability in filter alkalinity, resulting in correspondingly inaccurate predictions for spurious $SO_4^{=}$ formation. However, based upon the results discussed above, equation 1 provides a reasonably reliable means of estimating the significance of spurious $SO_4^{=}$ formation, under defined conditions.

To obtain an idea of the possible range in amounts of spurious $SO_4^{=}$ formation, plots of $\Delta SO_4^{=}$ vs. $Pso_2^{1/2} / (1-RH)^{1/3}$ have been constructed (18, 22). An example of this type of plot is given in Figure 1. Under usual Hi Vol sampling situations F ∿ 4.1 (1700 m^3 drawn through 410 cm^2) and A ∿ 0.3 (Gelman AE glass fibre filter), the concentration of spurious $SO_4^{=}$ would usually fall between 1 and 3 $\mu g/m^3$, assuming reasonable values for the parameters in equation 1.

In an attempt to evaluate the possible range in magnitude of the spurious $SO_4^{=}$ at a given site, $\Delta SO_4^{=}$ (min.) and $\Delta SO_4^{=}$ (max.) values were calculated for the site at 67 College Street in Toronto (downtown) for each month of the year. The resultant values are given in Table 3. As can be seen in Table 3, the amount of spurious $SO_4^{=}$ for this site is between 1 and 3 $\mu g/m^3$, with the higher values occurring in winter. Measured (31) $SO_4^{=}$ concentration maxima and minima in recent years at this site are ∿ 45 and 2 $\mu g/m^3$ respectively (annual arithmetic means ∿ 11 $\mu g/m^3$), with the lower values generally



* From reference 22

FIGURE 1 QUANTITY OF SPURIOUS $SO_4^=$ EXPECTED*

TABLE 3 MINIMA AND MAXIMA SPURIOUS $SO_4^=$ CONCENTRATIONS EXPECTED IN DOWNTOWN TORONTO*

	Pso_2 (ppb)†		RH (%)§		T (°C)**		$\Delta SO_4^=$ ($\mu g/m^3$)	
Month	Min††	Max	Min	Max	Min	Max	Min	Max
January	1	20	69	81	-8	-1	1.2	2.3
February	1	50	69	81	-7	0	1.2	3.0
March	1	20	62	78	-3	4	1.1	2.1
April	1	20	55	72	3	12	1.1	1.8
May	1	30	49	70	9	18	1.1	1.8
June	1	30	51	72	14	24	1.0	1.7
July	1	20	52	72	17	27	1.0	1.6
August	1	20	55	79	16	26	1.0	1.6
September	1	30	58	83	12	22	1.0	1.9
October	1	20	56	80	7	15	1.1	1.8
November	1	30	67	80	2	8	1.1	2.2
December	1	50	71	82	-5	1	1.2	3.0

* Obtained from equation 1 with $F \simeq 4\ m^3/cm^2$, $A \curvearrowright 0.32\ \mu\ eq/cm^2$, and $Z = 0$.
† 24-hour average, 67 College St. data from ARB/MOE.
†† Nominal detection limit.
§ Max. values are normal for 07:00; min. values are for 13:00.
** Values are min. or max. 24-hour average temperature for that month.

occurring in winter. With this in mind, together with the fact that the spurious $SO_4^=$ maximum occurs in winter, it is evident that for this site and for any others with a similar annual variation in $SO_4^=$ concentrations, the significance of spurious $SO_4^=$ will be greatest in winter, accounting for up to 100% of the measured $SO_4^=$ on "worst case" days.

Because of this potentially serious and variable interference in the determination of airborne $SO_4^=$ concentrations with glass fibre filters, a number of other filter materials have been tried, such as Teflon, polycarbonate and nylon membranes and cellulose ester (see Table 1). Although the Teflon and Nuclepore membrane-type filters virtually eliminate spurious $SO_4^=$ formation, they are not suitable for high volume air sampling because of the large pressure drop across the filter, which substantially increases the rate of pump motor wear. Furthermore, the flow across membrane-type

filters has been found to vary markedly with load, as well as being influenced dramatically by atmospheric conditions such as relative humidity (32). These large variations in flow could substantially bias a 24-hour sample, resulting in an average value which is substantially in error. For low volume sampling, however, Teflon filters would be suitable, as the flow problem is minimized and spurious $SO_4^=$ formation is virtually eliminated (17, 18, 22, 28, 37).

The cellulose-type filters have also been found to reduce greatly spurious $SO_4^=$ and are sufficiently porous to allow high volume sampling. Unfortunately, it has been found that this material adsorbs water vapour nearly irreversibly (33), rendering it unsuitable for determination of Total Suspended Particulate (TSP) matter. Worse, at least for the determination of airborne $SO_4^=$ concentrations, was the discovery that for one of the more widely used cellulose-type filters, Whatman 41, the initial capture efficiency for airborne particles is substantially less than for other frequently used filter types, as can be seen from Table 4. Also, it is evident from the data in Table 4 that Nuclepore-type filters are not well suited to the sampling of sub-micrometer airborne droplets or particles, and since a large portion of airborne $SO_4^=$ falls into this size fraction (2, 36), the use of these Nuclepore membranes is not advisable, despite reports that they do not promote significant spurious $SO_4^=$ formation (37). The filtration efficiency for glass and quartz fibre filters as well as for the Teflon membrane-type filters is very high and thus could be used without incurring significant losses due to particle or droplet penetration. However, the basic glass and quartz fibre filters can promote significant spurious $SO_4^=$ formation and thus are not preferred for sampling airborne $SO_4^=$.

Rigorous acid washing of quartz fibre filters has been found (2, 25) virtually to eliminate spurious $SO_4^=$ formation. However, the filters are very delicate and require special handling procedures, and thus are not suitable for routine use either for airbone $SO_4^=$ or TSP determinations.

The use of neutral quartz fibre filters, such as the Pallflex QAO, has been found (17, 21, 26) to reduce spurious $SO_4^=$ formation to $\leq$ 1 $\mu g/m^3$ ($\leq$ 4 $\mu g/cm^2$) but again, as with the acid-washed, strengthened, quartz fibre filters, the Pallflex QAO is extremely fragile and requires careful handling procedures. Consequently, for this practical consideration, this type of filter medium is probably unsuitable for larger scale monitoring networks.

In view of the results of previously reported work discussed above, the only filter medium that virtually eliminates spurious $SO_4^=$ formation and also meets the other requirements for high volume air sampling is the Pallflex TX40HI20WW (21, 26, 27). This

TABLE 4 FILTRATION EFFICIENCIES FOR SELECTED FILTER TYPES*

	Aerosol Type			
	Room Air Dust		H_2SO_4 Droplets $d \lesssim 0.3$ µm	DOP Droplets d = 0.2 µm
Filter Type	Face Velocity = 49 cm/s	Face Velocity = 147 cm/s	Face Velocity = 34 cm/s	Pressure Drop = 3 cm Hg
Pallflex 2500 QAO Quartz Fibre	-	-	98.5%	-
Gelman Microquartz	-	-	99.3%	-
Millipore Mitex pore = 5 µm	-	-	94.3%	∿92.0%(1)
Millipore Fluoropore pore = 3 µm	99.5%	97.0%	97.7%	-
Millipore Fluoropore pore = 1 µm	>99.9%	>99.9%	98.0%	>99.9%(2)
Ghia Teflo pore = 3 µm	-	-	95.5%	-
Ghia Teflo pore = 1 µm	-	-	98.5%	-
Ghia Zefluor pore = 1 µm	-	-	95.7%	-
Nuclepore pore = 0.8 µm	72.0%	89.0%	-	-
Nuclepore pore = 1.0	-	-	-	∿45.0%(3)
Nuclepore pore = 5.0	-	-	-	∿15.0%(4)
Whatman 41	64.0%	83.0%	-	-
Gelman Spectrograde	>99.8%	>99.8%	-	-
Gelman EPA Grade Glass Fibre	>99.8%	>99.8%	-	-
Gelman A Glass Fibre	>99.9%	>99.9%	-	-

* Data from references 25, 34 and 35.
(1) Face Velocity ∿ 10 cm/s
(2) Face Velocity ∿ 30 cm/s
(3) Face Velocity ∿ 60 cm/s
(4) Face Velocity ∿ 120 cm/s

filter has been found to have a high filtration efficiency, low flow resistance, good durability, insensitivity to relative humidity and low blank values for $SO_4^=$ (27). Thus, it appears that this type of filter would be suitable for use in larger scale high volume sampler networks for determination of the airborne sulphate load, keeping in mind that there has not yet been extensive experience with this medium by the various agencies responsible for large-scale, routine air sampling. There may be, for example, some unreported problems with this type of filter under certain sampling conditions which would limit its applicability.

Air Pollution Control Directorate (APCD) Results

As a consequence of the published reports of the problems associated with glass fibre filters, the APCD of the Environmental Protection Service, Environment Canada, initiated a study in 1978 to find a suitable alternative filter medium for the high volume air sampling of sulphates. During the 1978 and 1979 study periods, 11 types of filters were evaluated by means of side-by-side comparative sampling at a site in downtown Ottawa. The filters examined are given in Table 5.

TABLE 5 FILTERS EVALUATED IN 1978/79 APCD EXPERIMENTS

	Number of Samples Collected	
Filter Type	1978	1979
Gelman AE	20	28
Gelman Spectrograde	9	--
Gelman Microquartz	11	--
Gelman AN 3000	7	--
Gelman AN 1200	10	--
Pallflex TX40HI20WW	15	24
Pallflex 0X40HI	9	22
Pallflex 2500 QAST	18	28
Delbag Microsorban	18	--
Whatman 41	8	--
S & S HV1	--	27

As a check on the sampling and analytical methodologies used in this study, discs from seven replicate samples were analyzed for $SO_4^=$, TSP and Pb. The results are given in Table 6.

TABLE 6 REPLICATE SAMPLE RESULTS FROM 1978/79 APCD EXPERIMENTS*

Hi Vol No.	SO_4 ($\mu g/m^3$)	TSP ($\mu g/m^3$)	Pb ($\mu g/m^3$)
1	4.22	38	0.34
2	4.07	38	0.34
3	4.03	35	0.31
4	4.47	37	0.34
5	4.17	38	0.32
6	4.06	35	0.31
7	4.60	38	0.32
mean	4.23	37	0.33
σ	$\pm$0.22	$\pm$1.4	$\pm$0.01
Relative σ	$\pm$5%	$\pm$4%	$\pm$3%

* Obtained with a high volume sampler and a Gelman AE glass fibre filter, flow rate $\simeq$ 45 cfm (1.27 m^3/min).

As can be seen from the results in Table 6, the reproducibility of the sampling and analytical methodology for $SO_4^=$ is very good.

Blank filter determinations were also calculated for the filters studied in the 1978 experiments. The results are given in Table 7.

The results in Table 7 show that the blank $SO_4^=$ contribution to a result obtained with any of the fibrous filters was < 0.5 $\mu g/m^3$, with the exception of the Gelman Microquartz which gave a value of 0.8 $\mu g/m^3$. For the Pallflex TX40HI20WW, the blank value was < 0.2 $\mu g/m^3$, an insignificant amount for almost all applications.

Since, as discussed earlier, the Pallflex TX40HI20WW filter gives a negligible amount of spurious $SO_4^=$, it was decided that this would be the best choice for a reference filter. The results for each filter type were plotted against those obtained with the reference filter, and are shown in Figures 2 to 11. Also shown in each Figure is the equivalency or 45° line. Results obtained with the Whatman or membrane-type filters

TABLE 7 $SO_4^=$ FILTER BLANKS FOR 1978/79 APCD EXPERIMENTS

Filter Type	Filter No.	$SO_4^=$ ($\mu g/m^3$)*
Gelman AE	147	0.19
	197	0.19
Gelman Spectrograde	1129401	0.28
	1129425	0.34
Gelman Microquartz	600	0.78
	624	0.83
Gelman AN 3000	900	0.15
	922	0.19
Gelman AN 1200	800	0.15
	824	0.19
Pallflex TX40HI20WW	300	0.17
	323	0.14
Pallflex 0X40HI	400	0.47
	424	0.46
Pallflex QAST	500	0.17
	524	0.19
Delbag Microsorban	700	0.15
	724	0.23
Whatman 41	1100	0.14
	1124	0.14

* Based upon a 1700 m^3 air sample

were not plotted, as neither type is suitable for high volume sampling. From these Figures, it is clear that each of the filters tested resulted in the formation of spurious $SO_4^=$ to some degree, from very significant for the Gelman AE to rather small for the Pallflex 0X40HI, Delbag Microsorban and Gelman Microquartz.

To obtain a more quantitative picture of the capability of different filter types to form spurious $SO_4^=$, the mean concentrations of spurious $SO_4^=$ for each filter type and each study year were determined and are listed in Table 8.

The amount of spurious $SO_4^=$ for a filter was calculated by taking the difference between the $SO_4^=$ concentration obtained with the filter in question and that

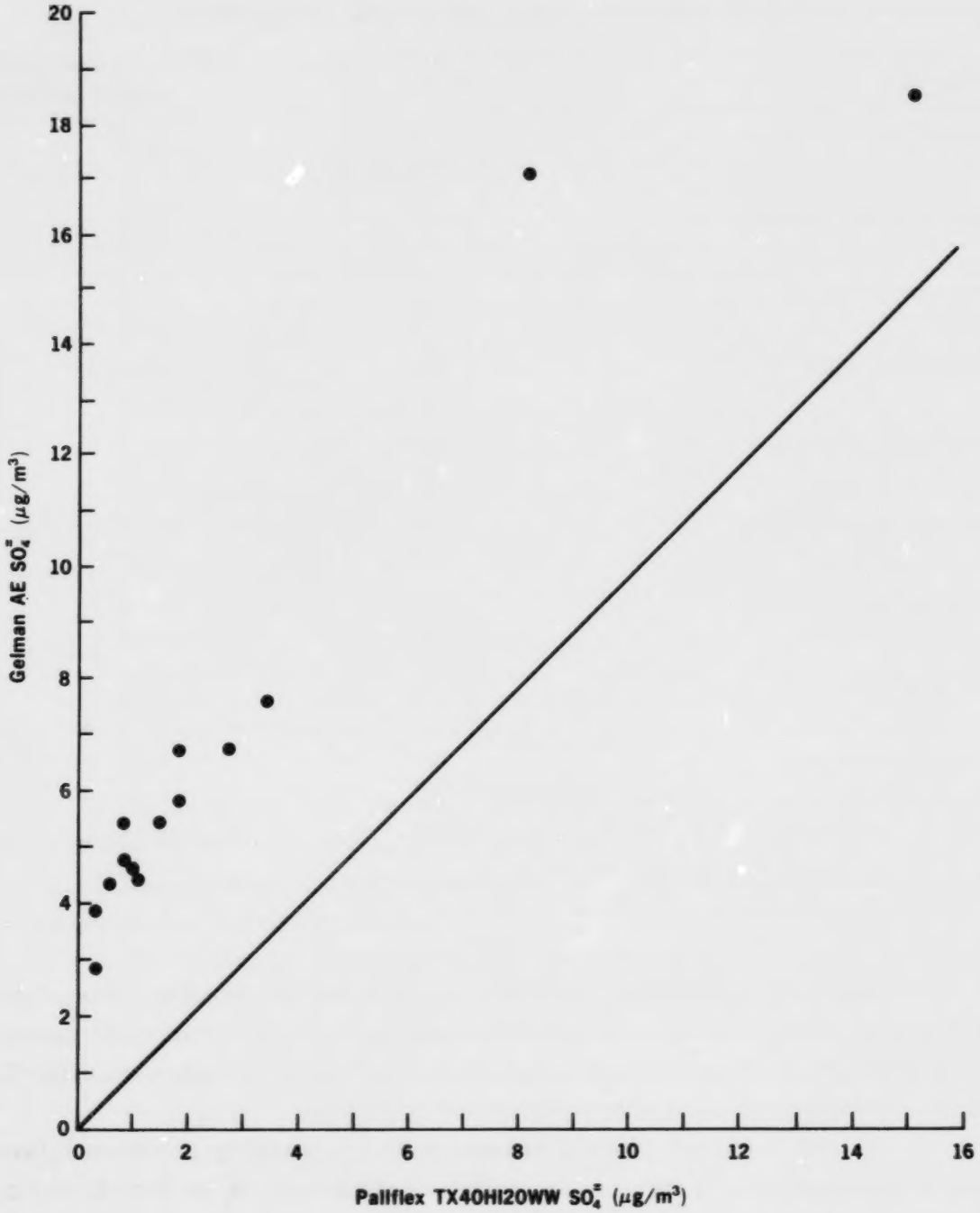


FIGURE 2 AIRBORNE $SO_4^=$ BY GELMAN AE VS. PALLFLEX TX40HI20WW, 1978

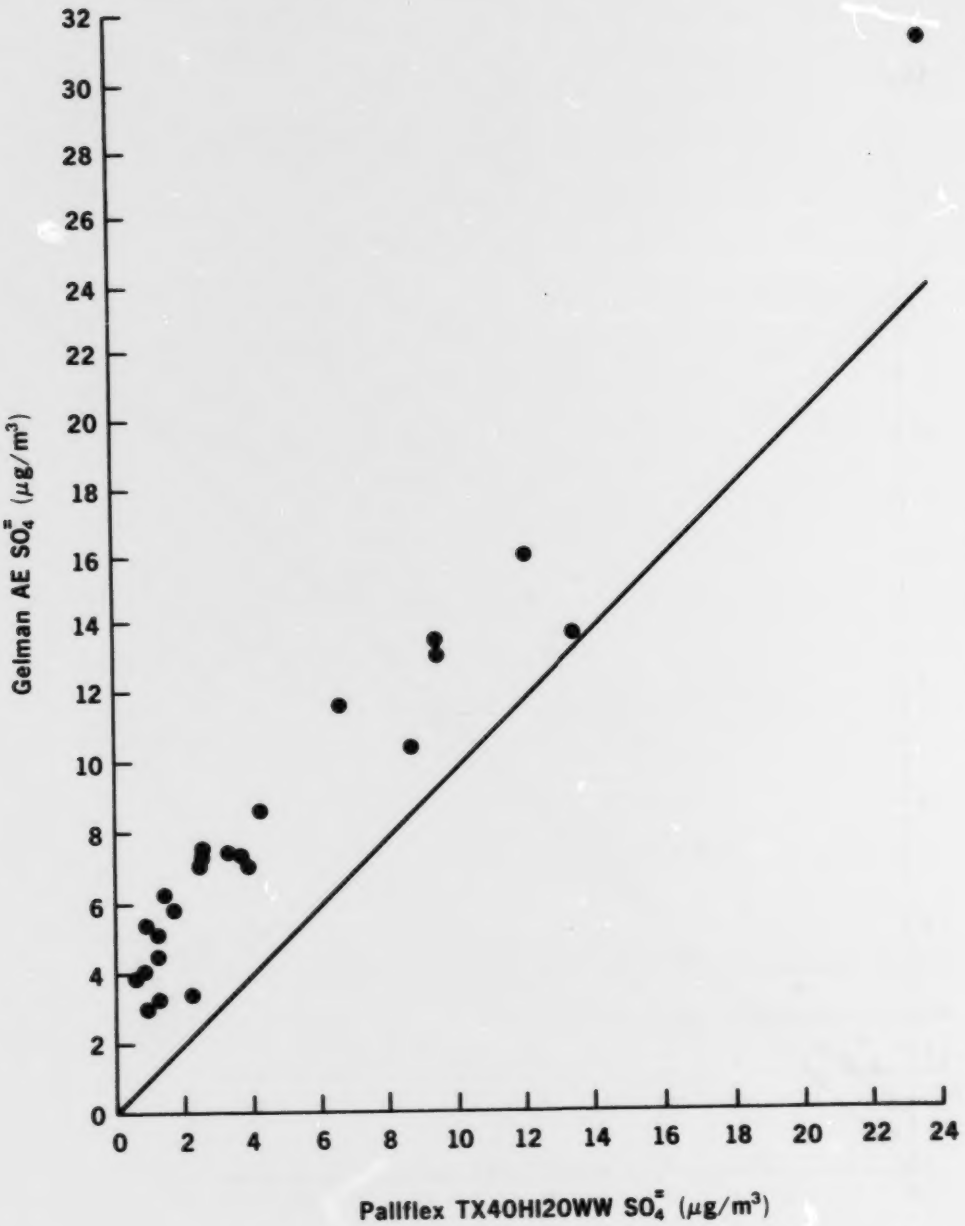


FIGURE 3 AIRBORNE $SO_4^=$ BY GELMAN AE VS. PALLFLEX TX40HI20WW, 1979

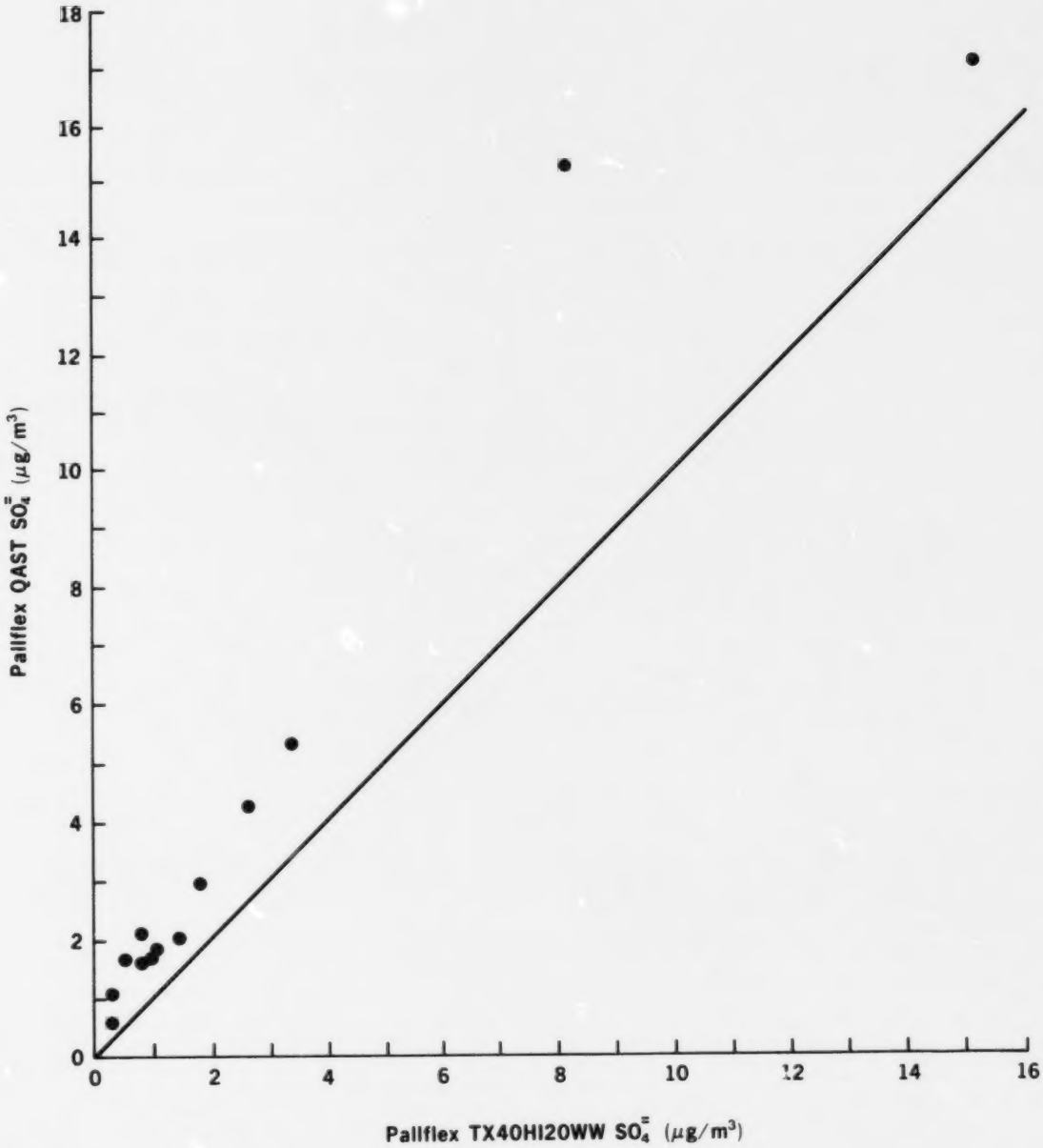


FIGURE 4 AIRBORNE $SO_4^=$ BY PALLFLEX QAST VS. PALLFLEX TX40HI20WW, 1978

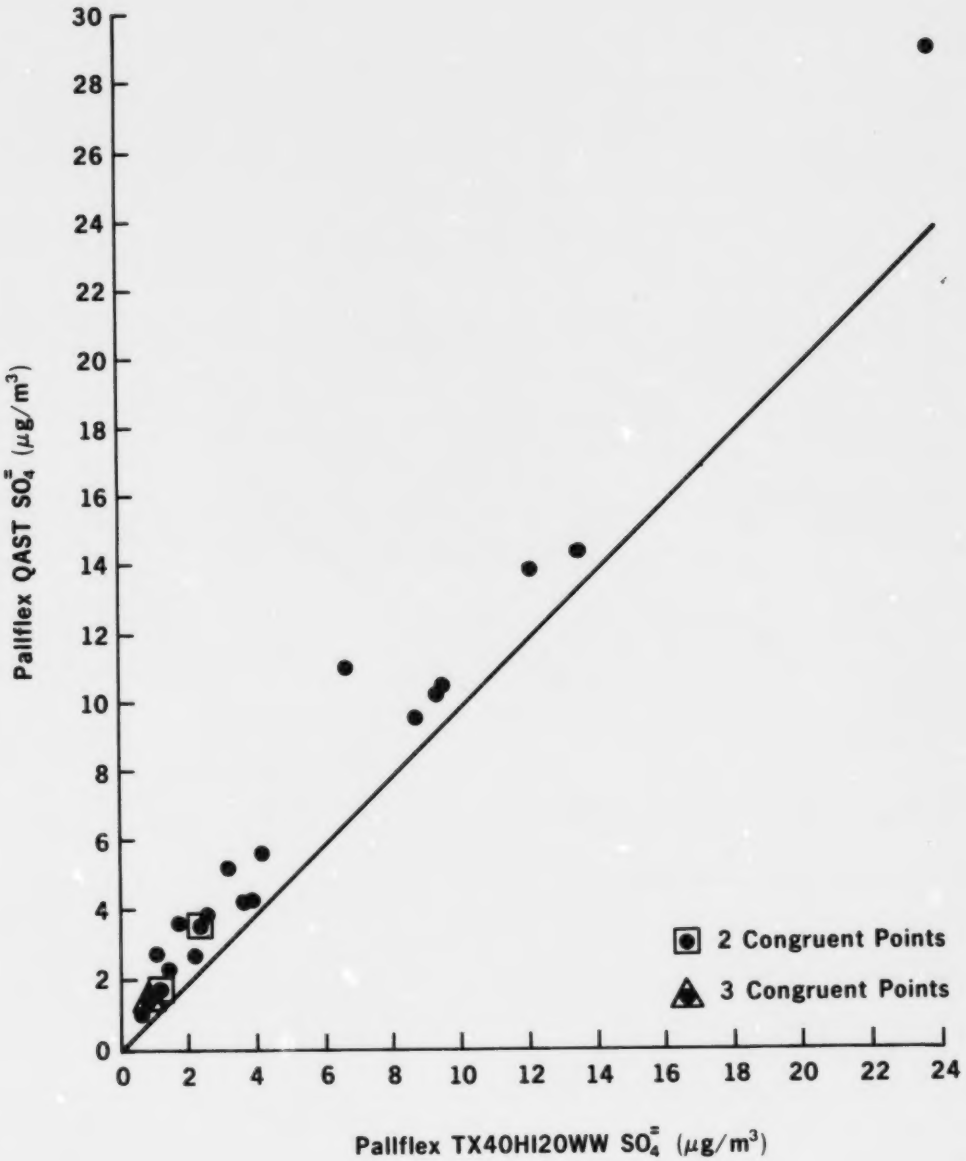


FIGURE 5 AIRBORNE $SO_4^=$ BY PALLFLEX QAST VS. PALLFLEX TX40HI20WW, 1979

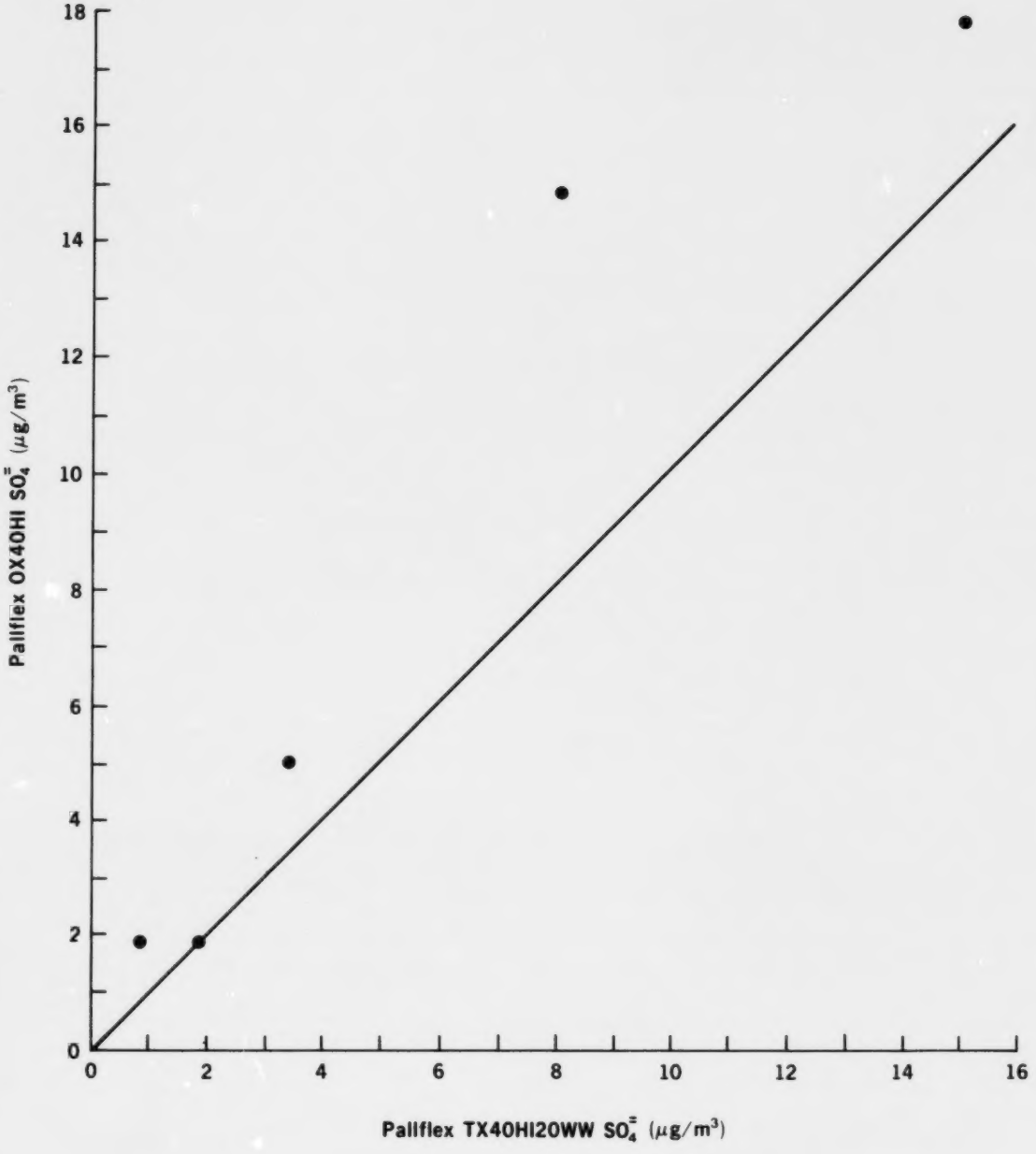


FIGURE 6 AIRBORNE $SO_4^=$ BY PALLFLEX 0X40HI VS. PALLFLEX TX40HI20WW, 1978

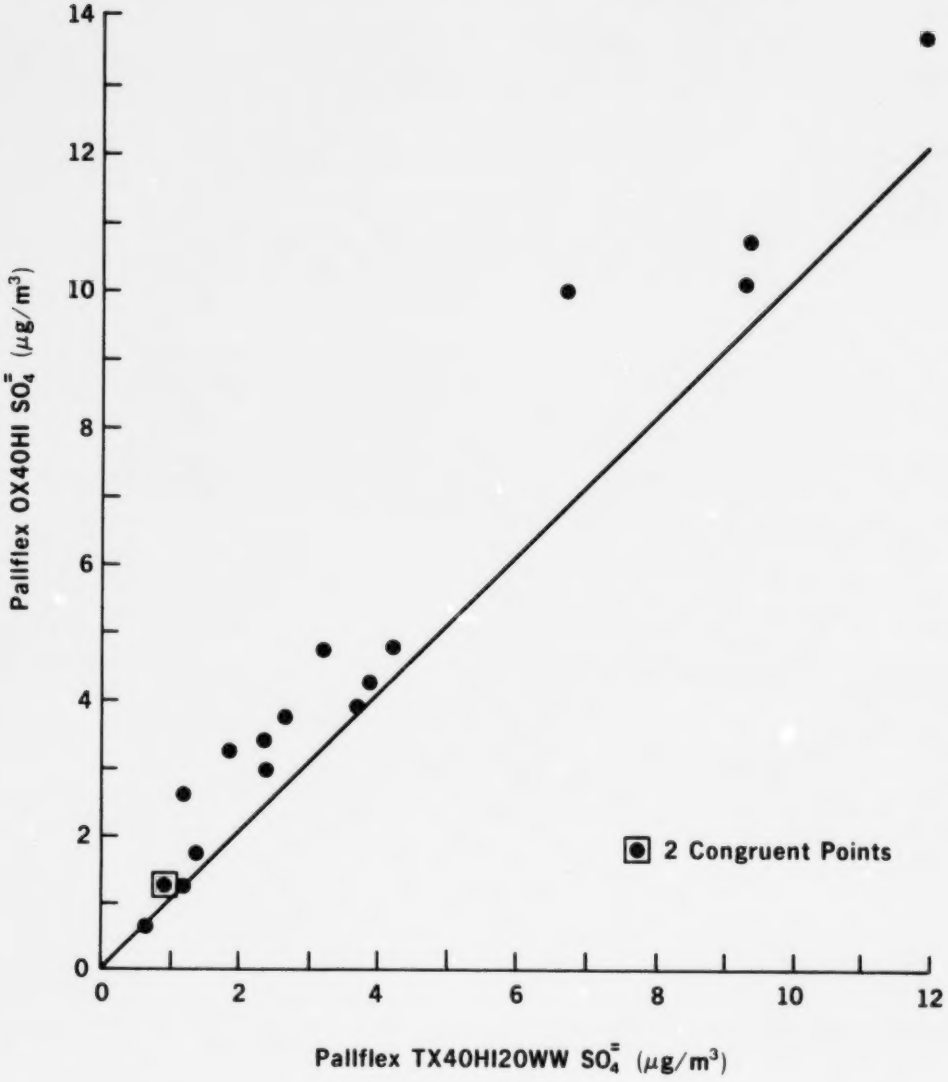


FIGURE 7 AIRBORNE $SO_4^=$ BY PALLFLEX 0X40HI VS. PALLFLEX TX40HI20WW, 1979

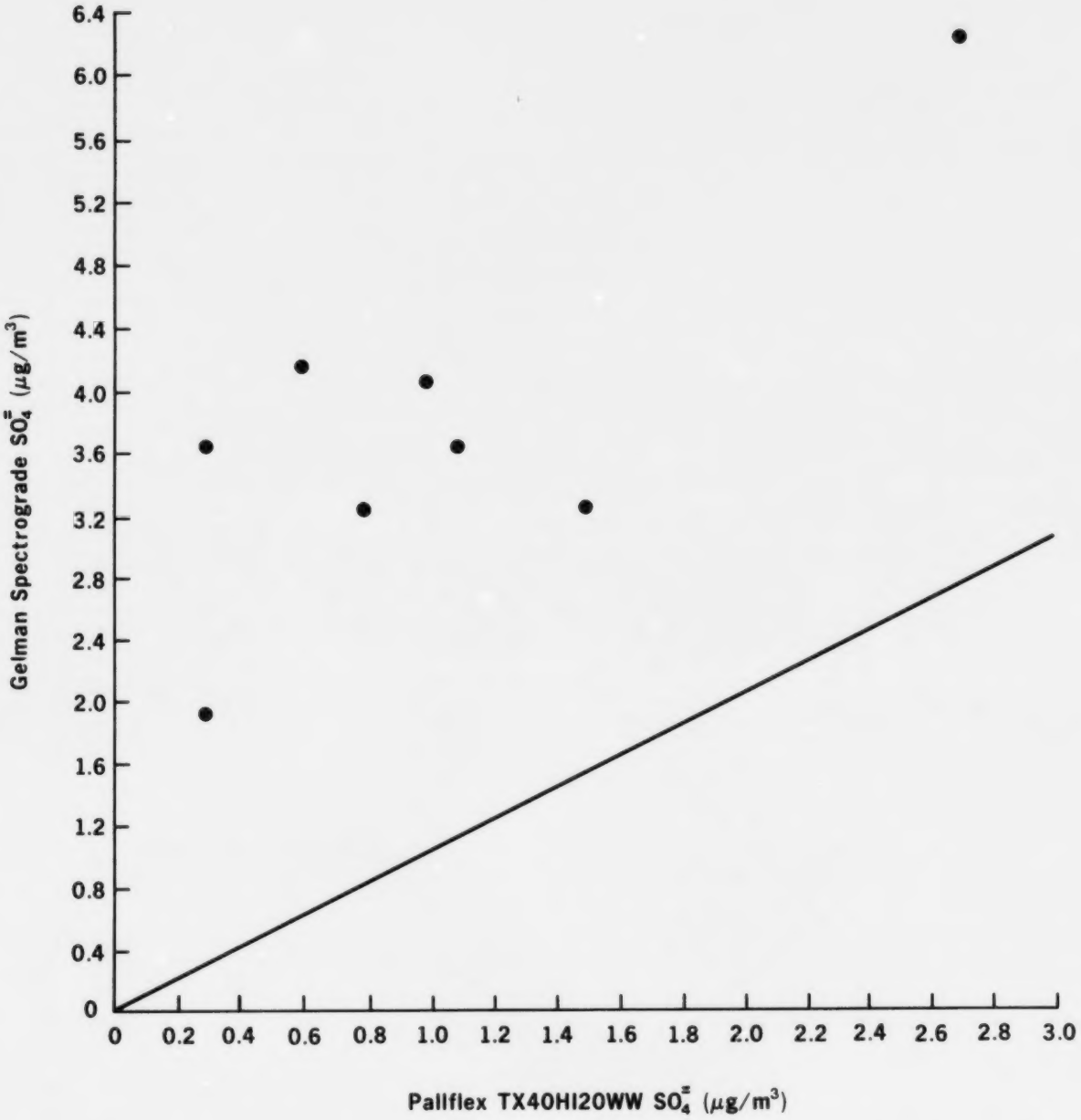


FIGURE 8 AIRBORNE $SO_4^=$ BY GELMAN SPECTROGRADE VS. PALLFLEX TX40HI20WW

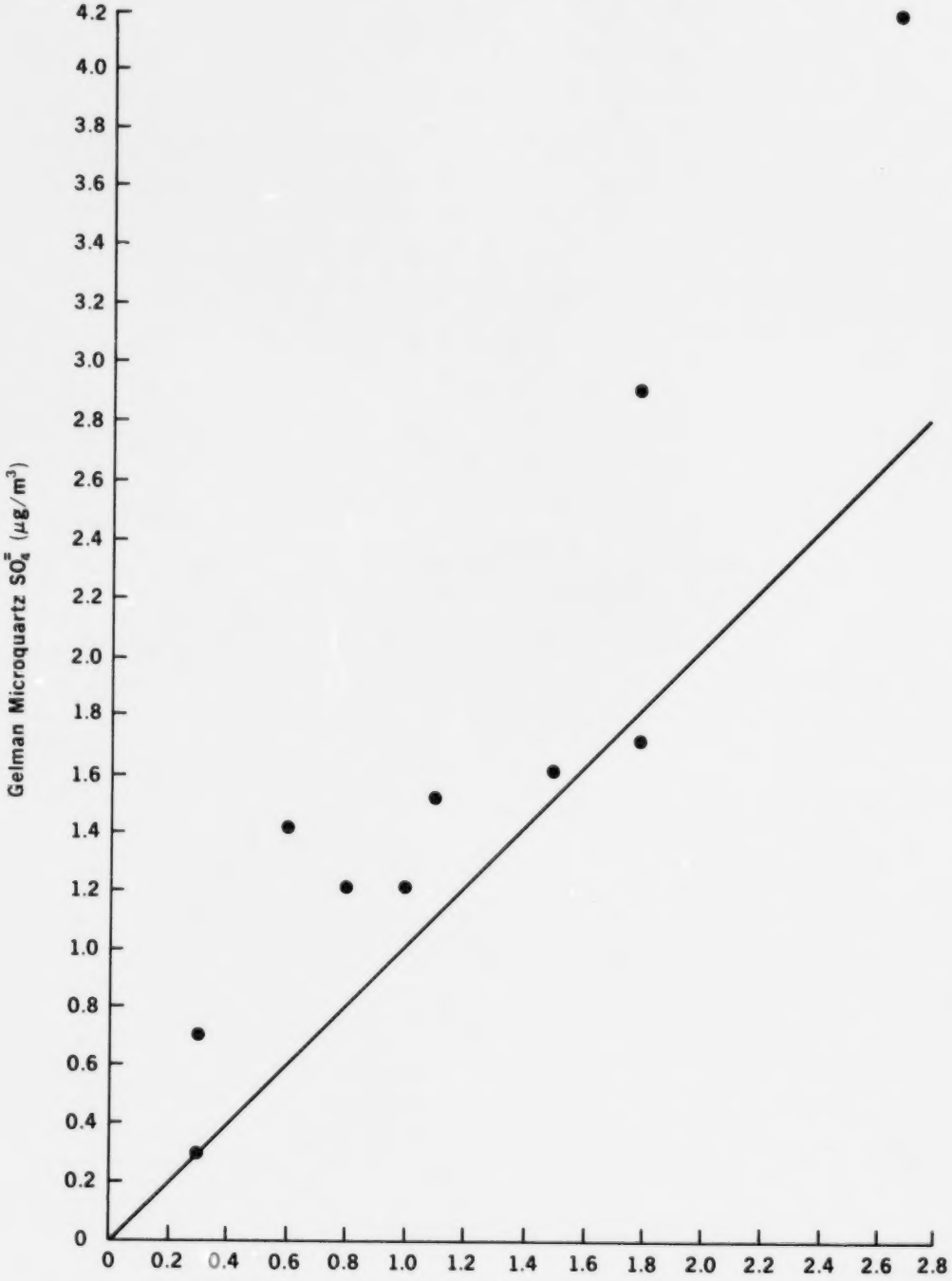


FIGURE 9 AIRBORNE $SO_4^=$ BY GELMAN MICROQUARTZ VS. PALLFLEX TX40HI20WW, 1978

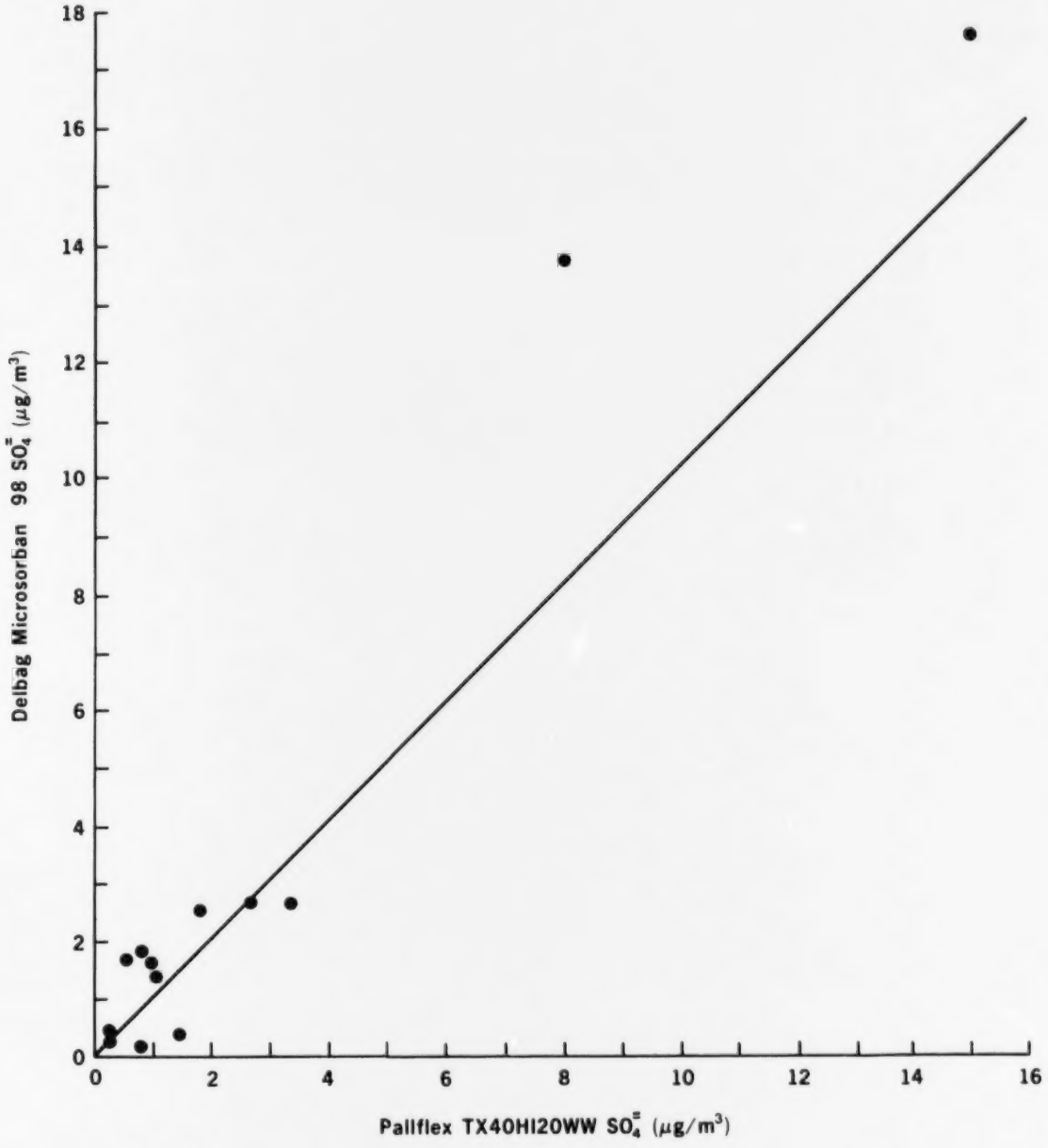


FIGURE 10 AIRBORNE $SO_4^=$ BY DELBAG VS. PALLFLEX TX40HI20WW, 1978

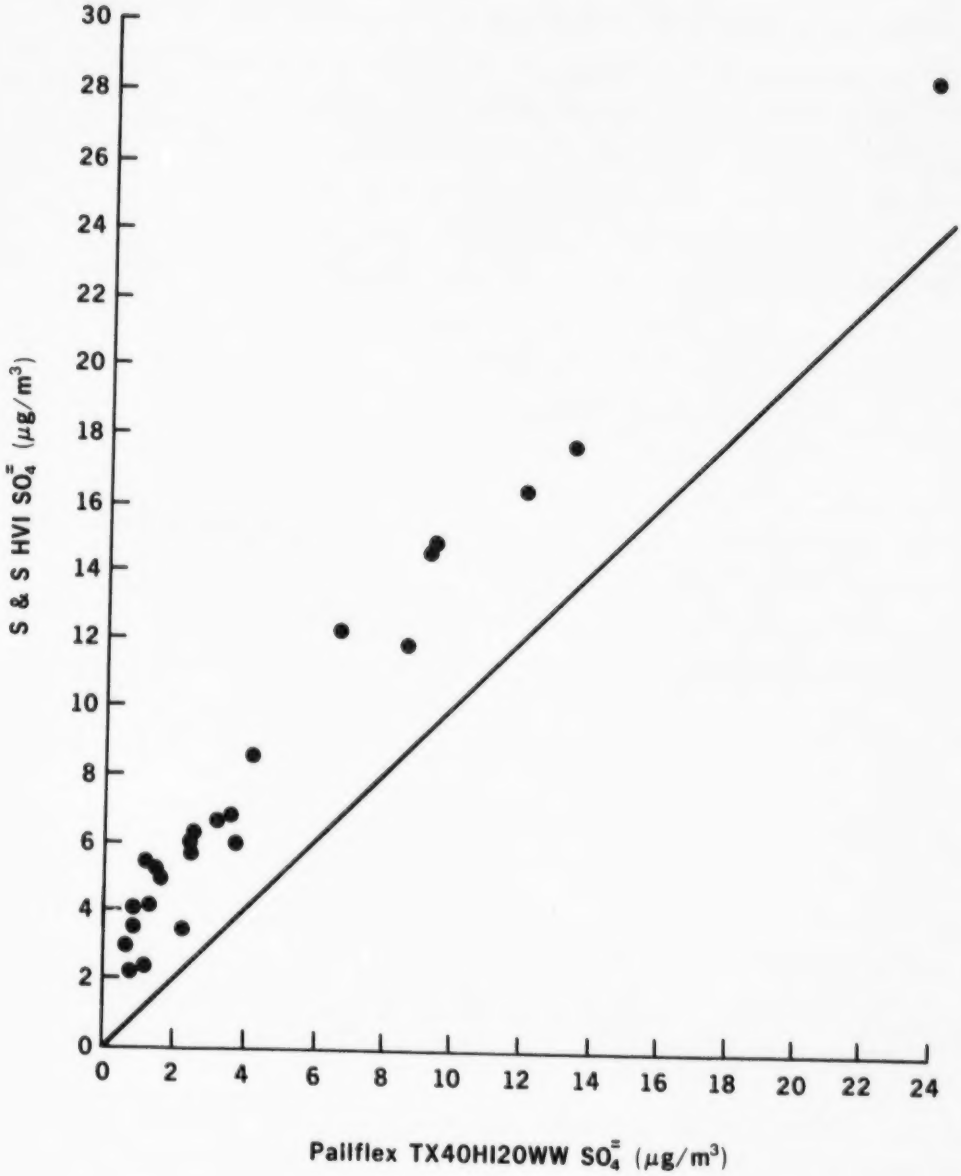


FIGURE 11 AIRBORNE $SO_4^=$ BY S&S HVI VS. PALLFLEX TX40HI20WW, 1979

TABLE 8 MEAN SPURIOUS $SO_4^=$ FOR THE DIFFERENT FILTERS EVALUATED*

Filter Type	1978	1979
Gelman AE	4.3 σ = 1.5 n = 14	3.73 σ = 1.52 n = 24
Gelman Spectrograde	2.0 σ = 1.15 n = 8	- - -
Gelman Microquartz	0.5 σ = 0.5 n = 10	- - -
Pallflex 0X40HI	3.0 σ = 2.6 n = 4	0.83 σ = 0.79 n = 18
Pallflex QAST	1.5 σ = 1.7 n = 13	1.33 σ = 1.25 n = 24
Delbag Microsorban	0.7 σ = 1.59 n = 13	- - -
S & S HVI	- - -	3.37 σ = 1.25 n = 24

* Mean spurious $SO_4^=$ =

$$\frac{(SO_4^= \text{ measured by filter "X"} - SO_4^= \text{ measured by Pallflex TX40HI20WW}}{n}$$

obtained with the Pallflex TX40HI20WW. This approach is based on the assumption that the Pallflex TX40HI20WW measures the "true" atmospheric $SO_4^=$ concentration, a valid assumption, in view of recent reports (21, 26, 27). The data in Table 8 show numerically what Figures 2 to 11 illustrate graphically, namely that the filters least prone to spurious $SO_4^=$ are the Gelman Microquartz, Delbag and Pallflex 0X40HI.

It is interesting to compare the mean spurious $SO_4^=$ obtained at the Ottawa site using Gelman AE filters with the range predicted by equation 1 (see Figure 1). It is

apparent that the spurious $SO_4^=$ obtained at this site is higher than would normally be expected, namely $\sim$ 4 $\mu g/m^3$ vs. a range of 1 to 3 $\mu g/m^3$. This is also higher than the range of 1 to 3 $\mu g/m^3$ which would be expected at the downtown Toronto site (67 College St.), using normals to estimate the range. This difference may be due to a batch of more alkaline filters being used in the 1978 and 1979 surveys, and/or possibly the ambient conditions (SO_2 concentration, RH) were atypical in a way that enhanced spurious $SO_4^=$ formation. It should be remembered that the formation of spurious $SO_4^=$ varies directly with filter alkalinity, other factors being kept constant (see equation 1).

Another aspect of the data obtained from the 1978 and 1979 experiments was the relationship between "true" $SO_4^=$ and TSP. This was calculated by comparing the $SO_4^=$ and TSP obtained with the Pallflex TX40HI20WW filter for each year.

Plots of TSP vs. $SO_4^=$ obtained from the Pallflex TX40HI20WW data are given in Figures 12 and 13 for the 1978 and 1979 data respectively. From these figures, it can be seen that there appears to be some sort of relationship between TSP and $SO_4^=$; however, the data from 1978 and 1979 studies are insufficient to allow an accurate determination of this relationship. For each year's data, a linear regression equation and correlation coefficients were developed and are included in Figures 12 and 13.

$SO_4^=$ Speciation

Because of the markedly different properties (e.g. toxicity) of different sulphate compounds (1), there have been several attempts in the past 10-15 years to develop a practicable method for determining the $SO_4^=$ compound distribution (speciation) in airborne particulate matter. Reviews of speciation have been reported previously (10, 11, 13) and a recapitulation of these reports will not be presented here. However, new results from previously reported methodologies will be discussed, together with promising new developments.

In 1975, Leahy et al. (38) reported a very promising, sequential, selective, solvent extraction scheme based upon the selectivity of benzaldehyde for H_2SO_4 and isopropanol for H_2SO_4 and NH_4HSO_4. However, more recent work has shown that although benzaldehyde is selective for H_2SO_4 doped clean Teflon or quartz fibre filters, it must be purified and carefully stored and handled to prevent interferences (39, 40, 41).

The recent work of Appel et al. (25) has made the suitability of this method extremely doubtful as they found, in controlled studies of extracting H_2SO_4 doped Teflon and quartz fibre filters loaded with previously collected particulate matter, that the

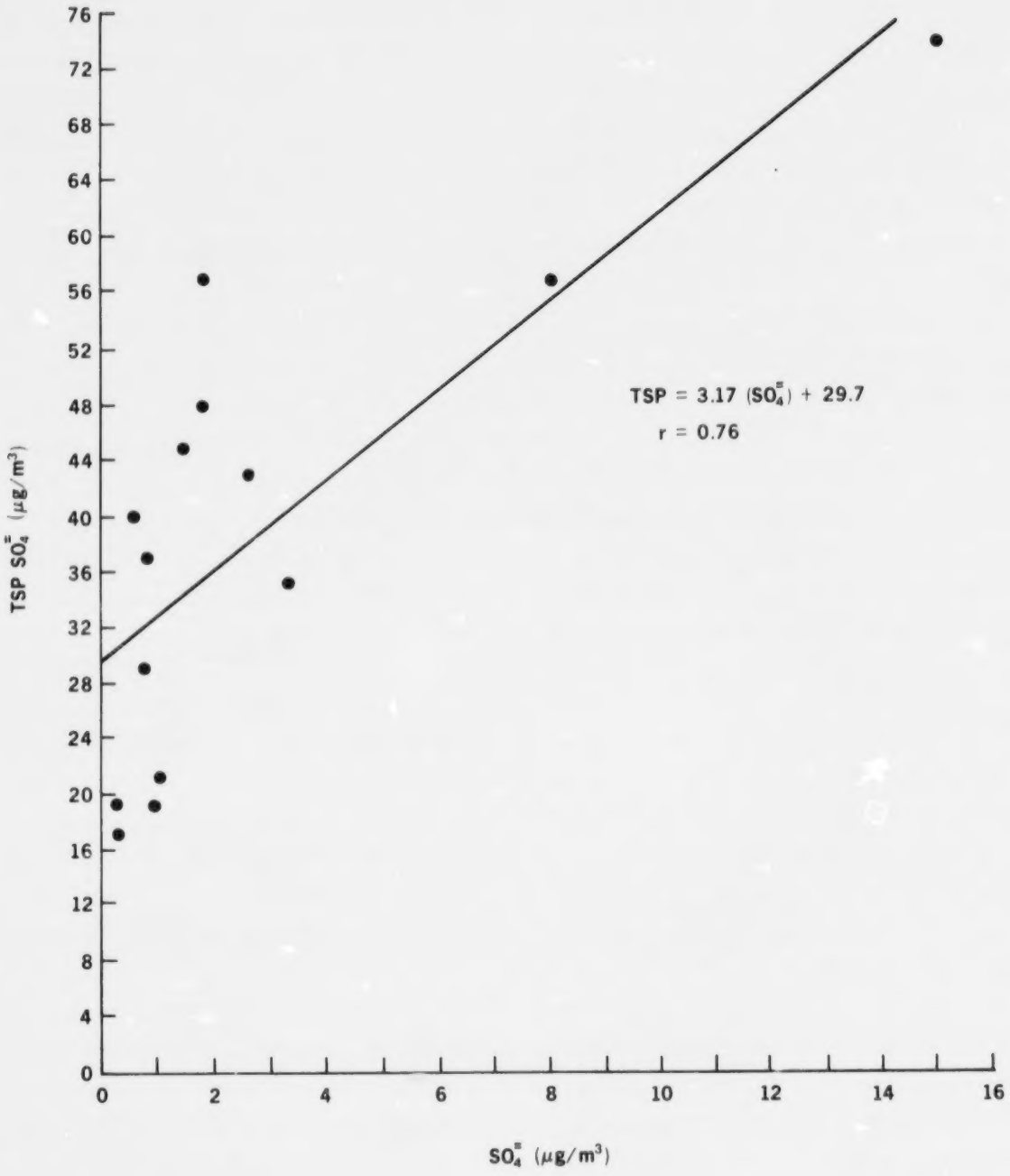


FIGURE 12 TSP VS. AIRBORNE $SO_4^=$ BY PALLFLEX TX40HI20WW, 1978

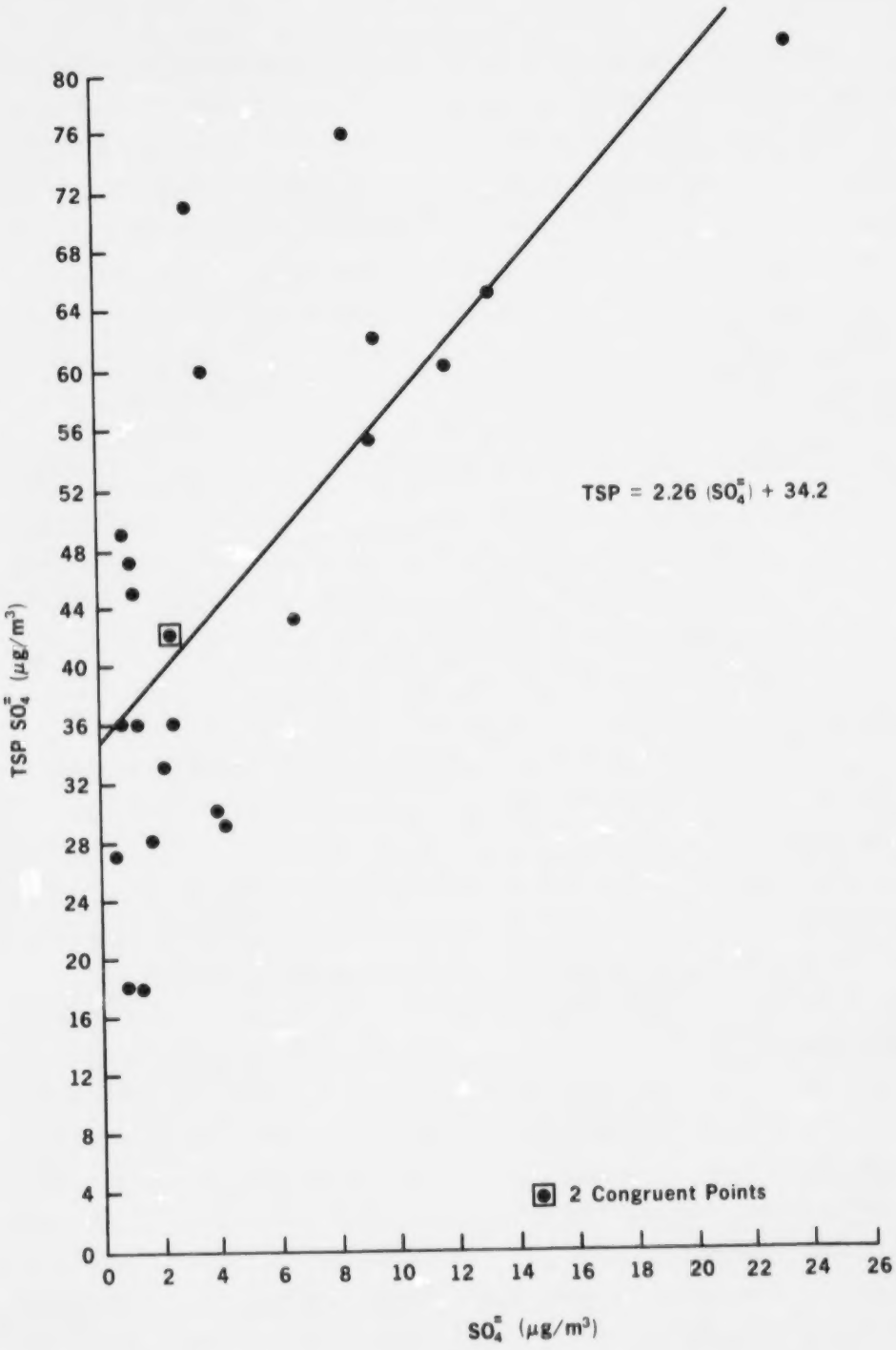


FIGURE 13 TSP VS. AIRBORNE $SO_4^=$ BY PALLFLEX TX40HI20WW, 1979

H_2SO_4 recovery was $\leq$ 30%. In fact, the results of this investigation throw into question the approach of attempting $SO_4^=$ speciation with a technique which involves, as a first step, filter collection of airborne particulate matter and, as subsequent steps, the obtaining of the $SO_4^=$ speciation, as this study has demonstrated the reaction of H_2SO_4 with co-collected particulate matter. For example, the observed results are consistent with the occurrence of the process illustrated by equation 2.

$$H_2SO_4 + (NH_4)_2\ SO_4 \rightarrow 2\ NH_4HSO_4 \qquad ...(2)$$

Another process that would be of importance under many sampling conditions would be:

$$H_2SO_4 + NH_3 \rightarrow NH_4HSO_4 \qquad ...(3)$$

The potential importance of this process can be appreciated - that in 1700 m^3 of air with an NH_3 concentration of 1 ppb ($\sim$ 0.6 $\mu g/m^3$), there is enough NH_3 to react with $\sim$ 6700 μg of H_2SO_4. This corresponds to $\sim$ 3.9 $\mu g/m^3$ H_2SO_4.

Thus, even if the selective solvent extraction scheme were entirely satisfactory, the occurrence of processes such as those given in equations 2 and 3 could put the results in considerable error.

A recently reported process (42) in which size-fractionated, NH_3 denuded samples of particulate matter are treated with ^{14}C labelled trimethylamine (TMA) looks promising for the measurement of H_2SO_4 and NH_4HSO_4 in air. The technique measures the airborne particle acidity, and the reported results from this technique correspond quite well with those obtained with a Gran-type titration described in an earlier report (36). The method has the potential of in situ reaction of the TMA with the particulate matter, thus eliminating the need for collection of the particulate matter on filters. It cannot, however, distinguish between H_2SO_4, NH_4HSO_4, $(NH_4)_2SO_4$ and other metal sulphates.

A technique based upon the flame photometric detector (FPD) has recently been described (43). This would potentially allow the determination of airborne H_2SO_4 and the total (NH_4HSO_4 + $(NH_4)_2SO_4$) with a time resolution of about 10 minutes. The detection limit for H_2SO_4 is $\sim$ 4 $\mu g/m^3$, when the total airborne sulphate concentration is 20 $\mu g/m^3$. The technique is still in the developmental stage and future improvements are likely; if they materialize, they will allow the near "real time" measurement of H_2SO_4 and (NH_4HSO_4 + $(NH_4)_2SO_4$) in air.

3 SAMPLING FOR AIRBORNE PARTICULATE NITRATES

Within the past four years, many reports (19, 21, 22, 24, 26, 27, 44, 46, 47, 48, 50, 51, 52, 54, 55, 56, 57, 59) have described interferences, positive and negative, that are incurred in the sampling of airborne particulate nitrates. The filters evaluated as well as the type of study undertaken by the various investigators are given in Table 9. The first report that suggested problems with the commonly used glass fibre - high volume sampling method for airborne particulate nitrates was made by Spicer (60), who found that nitrate (NO_2^-) data obtained from neutral quartz fibre filters were substantially lower than those obtained with the more alkaline glass fibre filters. This was followed by a report (52) which gave evidence of the volatilization of HNO_3 from collected particulate nitrate as a result of the reaction of co-collected H_2SO_4 with the particulate NO_3^-. This phenomenon would result in a negative interference, or "negative artifact", in the determination of the airborne particulate nitrate.

Within two years, two publications followed (19, 54) which documented substantial differences in the atmospheric NO_3^- results obtained with different types of filter media. These findings were further confirmed by a number of investigators (see references referred to above).

The cause of the positive interference "positive artifact" is almost entirely due to the adsorption of HNO_3 and the conversion of NO_2 to NO_3^- by the filter medium. This has been documented by several investigators, with more comprehensive investigations being described in references 22, 24, 46, 47 and 56. An estimate of the maximum possible quantity of artifact NO_3^- to be found with different filter media can be obtained from the data of Appel et al. (22). These are given in Table 10, from which it can be seen that glass and cellulose ester fibre filters have sizeable collection efficiencies for airborne HNO_3 and, consequently, are susceptible to significant spurious NO_3^- contributions to the determination of airborne particulate NO_3^-.

When reviewing Table 10, it should be borne in mind that concentrations of spurious NO_3^- are the upper limits, as co-collected acidic particulate matter would diminish, to some extent, a filter's capacity to capture HNO_3 (44). Also, if the atmospheric concentration of HNO_3 in the area sampled is insignificant, then the importance of the artifact would be correspondingly diminished. Atmospheric sampling in the South California Air Basin has yielded NO_3^- data consistent with the results indicated in Table 10. For example, Witz and MacPhee (19) found that the atmospheric NO_3^- data

TABLE 9 SUMMARY OF FILTERS EVALUATED AND VARIABLES STUDIED FOR THE SAMPLING OF AIRBORNE NO_3^-

Variable Studied	References										
Filter	Comparative Atmospheric Sampling	NO_2 Concentration	NO Concentration	HNO_3 Concentration	Temperature	Relative Humidity	O_3 Concentration	NH_3 Concentration	H_2SO_4 Concentration	PAN Concentration	Particulate Catalysts
Gelman AE	44,24,45,46, 19,20	24		24		46				24	24,46
Gelman EPA	44,47,54,19	22,56		22	22,56	22,56	22,56	22,56		24	
Gelman Spectrograde	24,44,22,56,19	24,22,47,56		24,22	22,56	24,22,56	22,47,56	22,56	52	24,46,53	47
Gelman A	24,22,47,50, 54,26,19,55,56	24,46,22,47,56	47	24,46,22	22,47,56	24,22,47,56	22,47,56	24,46,22,56		24	
Gelman AA	24	24		24		24,46				46	24,46
Gelman Microquartz	24,44,54,21	24,47		24		24,46,47	46				
Gelman GH-1	56	22,56		22	22,56	22,56	22,56	22,56			
Gelman E	24	24,46		24,46		24		24,46		24,46	
Pallflex QAO	44,50,25,26			48,49		49					
Pallflex QAS									49	24	24,46
Pallflex QAST	24,54,20	24		24		24					
Pallflex TX40HI20WW	44,21,27,26,20									24	
Pallflex E70-2075W		24		24		24,46	47	24,46		24,46	
Millipore Mitex		46,47		24,46				24,46,25		24,46	
Millipore Duralon	24	24,46,25		24,46,48,55		24					
Millipore FALP				53							
Millipore Fluoropore	22,50,56,26	22,56		22	22,56	22,56	22	22,56			
Millipore Celotate		24,46		24,46				24,46		24,46	24,46
Whatman 41	22,47,50,56, 20,57	22,47			22,56	22,56	22,47,56	22,56			
Whatman Glass Fibre				55							
Ghia Zefluor	50,55			55					50		55
Ghia Nylon	50				22,56	46	22,56	22,56			
MSA 1106 BH	22,56	22,56					47	24,46		24,46	
Nuclepore	57	46,47		24,46							
Toyo Cellulose											
S & S Fast Flow 2W/Nacl		48,49		48,49		49					

TABLE 10 MAXIMUM SPURIOUS NO_3^- FOR DIFFERENT FILTERS*

Filter Type	Spurious NO_3^-			
	$\mu g\ NO_3^-$ per 47 mm filter ($\sim$ 15 cm^2)	$\mu g\ NO_3^-$ per 25 x 20 cm^2 filter ($\sim$ 410 cm^2)	$\mu g/m^3$ (1700 m^3 Volume)	$\frac{NO_3^-\ X}{NO_3^-\ F}$
Fluoropore (F)	32.2	880	0.52	1.0
Gelman A	516	14 104	8.3	16.0
Gelman GA-1	733	20 035	11.8	23.0
Whatman 41	741	20 254	11.9	23.0
MSA 1106B H	1 223	33 429	19.7	38.0
Gelman EPA	1 475	40 317	23.7	46.0
Gelman Spectrograde	1 681	45 947	27.0	52.0

* Based upon the quantity of NO_3^- adsorbed per filter from an air stream containing 0.2 ppm HNO_3 at 50% RH T = 22°C; $\sim$ 13.5 m^3 air sample, total NO_3^- in air stream $\sim$ 6900 µg. From reference 22.

obtained with different filter media fell in the order: Gelman Spectrograde > Gelman AE > Gelman EPA > Gelman A, with the Spectrograde collecting, on average, 219% of that obtained with the Gelman A filter. More recent data (21) for spurious NO_3^- for this region show the average amount to be $\sim$ 9 $\mu g/m^3$, when using a glass fibre filter (Whatman EPM 1000). These results are consistent with the data of Spicer and Schumacher (46) who found the amount of spurious NO_3^-, when sampling with a glass fibre filter (Gelman A), to be $\sim$ 7 $\mu g/m^3$ for the equivalent of a 1700 m^3 air sample.

As mentioned above, atmospheric NO_2 can also lead to spurious NO_3^- on certain filter media. Generally, it has been found that the amount of spurious NO_3^- formation due to NO_2 is less significant than that due to the adsorption of HNO_3 (22, 24, 46, 56). For example, the work of Appel et al. (22, 56) has shown that even under rather extreme conditions ((NO_2)= 500 ppb, RH = 50%, 13.5 m^3 air sample), the amount of spurious NO_3^- was $\sim$ 2 $\mu g/m^3$ for the most alkaline filters. If the sample volume were increased to something approaching the usual ($\sim$ 1700 m^3), the importance of the artifact would no doubt be reduced substantially. The addition of an artificially high (for Canada at least) concentration of O_3 (500 ppb), together with increasing the relative humidity to 90%, resulted in less than 10 $\mu g/m^3$ of spurious NO_3^-, based upon a 13.5 m^3 air sample.

Thus, the conversion of NO_2 to NO_3^- does not make a large contribution to the spurious NO_3^- formation.

The relative importance of HNO_3 and NO_2 in the formation of spurious NO_3^- on various filter media can be readily appreciated by reference to Table 11. As an approximation, HNO_3 is 100 times more efficient than NO_2 in spurious NO_3^- formation. In atmospheric sampling, the relative importance of NO_2 and HNO_3 will depend upon their respective concentrations. Although NO_2 is monitored routinely in many urban centres across Canada, data on typical HNO_3 concentrations are non-existent. However, based upon the recent work of Spicer and his colleagues in the U.S.A., a reasonably reliable estimate of the HNO_3 concentration can be obtained from the prevailing ambient NO_2 concentrations, namely $(HNO_3) \sim 5\% (NO_2)$ (58). If this approximation turns out to be generally valid, then, together with the data of Table 11, it is clear that HNO_3 is the greater contributor to spurious NO_3^- formation.

TABLE 11 FILTER CONVERSION EFFICIENCIES*

Filter Type	500 ppb NO_2† 50% RH T = 20°C V = 13.5 m^3	200 ppb HNO_3 50% RH T = 22°C V = 13.5 m^3
	%	%
Fluoropore	0.02	0.5
Gelman GA-1	0.15	11.0
Whatman 41	0.16	11.0
Spectrograde	0.11	24.0
Gelman A	0.17	7.4
MSA 1106 BH	0.18	18.0
Gelman EPA	0.18	21.0

* Calculated from reference 22.

† Based upon assumption that 13.5 m^3 of 500 ppb NO_2 contains 275 μ moles NO_2 which would yield 275 μ moles NO_3^-.

Consistent with this forecast, Appel et al. (22, 56) found that the NO_3^- concentration results obtained with high volume ambient air samples exhibited the same

rank ordering as the spurious NO_3^- formation due to HNO_3 adsorption, whereas the rank ordering of filter-induced NO_2 to NO_3^- conversion was markedly different.

Other atmospheric variables (e.g. SO_2, NH_3, RH, T) have also been evaluated (22, 24, 46, 56), as have gas filtrate interactions, (24,46), for their potential to augment spurious NO_3^- formation. Generally, the HNO_3 capture efficiency increased with RH and decreased with temperature. Sulphur dioxide, ammonia or co-collected particulate matter did not have a significant effect.

Although the NO_3^- concentration determined with various filter media had the same rank ordering as HNO_3 adsorption by the filters, and the NO_2 contribution to the measured NO_3^- concentration was probably minor, it is still not possible to determine reliably even the minimum airborne particulate NO_3^- values (Table 9) from the observed values). This is because of the competing process of HNO_3 volatilization as a consequence of the reaction of co-collected H_2SO_4 with the particulate NO_3^- (52). Harker and his colleagues observed a five-fold reduction in NO_3^- when H_2SO_4 was co-collected with a Gelman Spectrograde glass fibre filter. A similar result was obtained by Forest et al.(49) who observed up to $\sim$ 70% loss of particulate NO_3^- collected on quartz filters when exposed to air containing H_2SO_4 droplets at a concentration of 2 to 10 $\mu g/m^3$. Also, the passage of 7 m^3 (flow = 20 L/min) of NH_3 and HNO_3 free air at 21°C through a Teflon filter loaded with known amounts of NH_4NO_3 resulted in a loss of 45 $\pm$ 11% of NO_3^- from the filter.(55) This is not surprising, in view of the equilibrium represented by equation 4.

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3 \qquad \ldots.(4)$$

The equilibrium constant (Kc) for equation 4 has been found to be represented by equation 5(61) where T is the temperature in degrees K.

$$\ln Kc = 62.296 - \frac{21510}{T} \qquad \ldots.(5)$$

This relationship was recently investigated again and essentially confirmed (62). Using equation 5 with a temperature of 25°C, a value of $\sim$ 7 ppb for the equilibrium vapour concentration of NH_3 or HNO_3 is obtained. Thus, if NH_3 and HNO_3 free air is drawn through a bed of NH_4NO_3 on a Teflon filter, thermodynamics alone dictate a volatilization of the NH_4NO_3. How significant this process would be in atmospheric sampling situations would depend, to a large extent, on the effect of

co-collected particles on the equilibrium and the kinetics of the vapourization process, and on the prevailing temperature and the ambient air concentration of NH_3 and/or HNO_3. From equations 4 and 5, it can be seen that the volatilization process would be enhanced by increasing temperature, and inhibited by increasing air concentrations of NH_3 and/or HNO_3. At 25°C, the equilibrium vapour pressure of 7 ppb for NH_3 and HNO_3 exceeds that likely to be found in many if not most sampling circumstances in Canada and, consequently, the volatilization due to vapour pressure alone would occur to some extent. However, when sampling with glass fibre filters, at least some of the NHO_3 vapour would be captured by the filter itself, thus reducing, or possibly eliminating, the potential loss. Consequently, because of the conflicting nature of the above processes, it is difficult, if not impossible, to evaluate the significance of this "negative artifact" mechanism for 24-hour, high volume ($\sim$ 1700 m^3 air sample) sampling.

Recent work by Appel et al.(63) has shown that for at least some sites and conditions (total inorganic $NO_3^- \leq 100\ \mu g/m^3$, sample volume $\leq 12\ m^3$), Gelman A glass fibre filters function as a total inorganic nitrate (TIN) sampler. TIN equals HNO_3 + particulate NO_3^-. It is doubtful that this low volume result can be applied to results from high volume air samples containing more than $\sim$ 8.3 $\mu g/m^3$ TIN in view of the Gelman A's finite capacity to adsorb HNO_3 (see Table 9) and the fact that co-collected H_2SO_4 would result in the volatilization of at least some NO_3^- as HNO_3(52).

The fact that glass fibre filters collect vapour phase inorganic nitrate (i.e. HNO_3) as well as particulate NO_3^- will result in an error in the TSP value obtained by the usual Hi Vol method. The size of the error introduced will vary and will depend upon the prevailing air concentrations of HNO_3 and H_2SO_4. As mentioned above the HNO_3 would result in a positive error in the TSP determination while the co-collected H_2SO_4 would have a counter-effect in that it would volatilize a certain portion of the collected particulate NO_3^- and HNO_3. The maximum possible error due to the collection of airborne HNO_3 would be 2.5 $\mu g/m^3$ per ppb of HNO_3 in the sampled air. Although no data are currently available, the 24-hour average concentration of HNO_3 in most Canadian urban airsheds is less than 3 ppb (< 7.5 $\mu g/m^3$). Thus, the error introduced into the TSP determination must be less than or equal to this value (7.5 $\mu g/m^3$).

A recent report by Appel and Tokiwa (64) shows that the presence of moderate amounts of strong acid (H_2SO_4 or HCl) in the atmosphere can induce up to 95% loss of collected NO_3^- from Teflon filters. Also, the work of Harker et al. (52) demonstrated that significant NO_3^- losses can occur from glass fibre filters. A similar result was obtained by

Pierson et al. (26) with Teflon filters and by Forrest et al. (49) with quartz fibre filters. Therefore, at present, it is not possible to determine reliably the significance of the various "negative" and "positive" artifacts for atmospheric NO_3^- concentrations obtained with glass or quartz fibre or Teflon membrane filters.

The TIN could be determined in a high volume sampling situation by using a NaCl impregnated cellulose backup filter in combination with a fore filter (quartz, glass fibre or Teflon). Sodium chloride impregnated cellulose filters have been shown (49,55) to be very efficient collectors of HNO_3. The aft filter would thus capture any HNO_3 that might get past the fore filter. Analysis of both the fore and aft filters for NO_3^- would be needed to obtain the TIN.

If a low volume sampling train were to be used, then a Teflon fore filter followed by either a nylon or NaCl impregnated cellulose aft filter could be used to obtain the TIN (46,48).

4 ANALYTICAL METHODS

One objective of this project was to review and summarize a number of previously reported comparative analytical methodologies for $SO_4^=$ and NO_3^-.

4.1 $SO_4^=$ Analytical Methods

The experimental evaluations of the analytical methods for $SO_4^=$ that were reviewed are contained in Table 12. This review is not exhaustive as there are other experimental evaluations, not included here, that have been carried out and reported. The methods evaluated here, however, are among those most frequently used for the analysis of aqueous samples for $SO_4^=$ and the experimental evaluations reviewed were particularly thorough and carefully executed.

TABLE 12 SUMMARY OF $SO_4^=$ ANALYTICAL METHODS REVIEWED

Method	References
Methylthymol Blue (MTB)	65, 6, 68, 49, 71, 72
Brosset Modified Thorin	66, 67
Turbidimetry (SulfaVer IV Method)	44, 68, 69
Barium Chloranilate	66
XRF	66, 36
AIHL Microchemical	66, 69, 70
Turbidimetry (AIHL Methods)	68, 69
Ion Chromatography (IC)	68, 69, 36, 71, 72

An important consideration in this review is the performance of the automated methods relative to the manual ones. This is important in applications which involve a large number of samples, such as aqueous extracts of filters from large-scale high volume sampling networks.

If one assumes that the airborne sulphate concentrations for most sites fall within the range of 2 to 20 $\mu g/m^3$ almost all of time, extraction of 10% of the exposed filter with 50 mL of water would result in extracts in which the $SO_4^=$ concentration falls in the range of 6.8 to 68 $\mu g/mL$.

An examination of Table 13 reveals that either the MTB, turbidimetric or IC methods could be used for a solution in this concentration. Of the two methods that can be automated (MTB and IC), IC has been found (69) to be slightly more accurate and precise in this range ($\sim$ 7 to 70 µg/mL). Whether or not this improvement justifies the cost involved in switching from an operational MTB method to an IC procedure depends largely upon user requirements. For the determination of $SO_4^=$ from high volume air samples, the data obtained from the MTB method would be satisfactory for virtually all air pollution monitoring purposes.

However, if the air particulate samples were obtained from a low volume sampler (e.g. dichotomous sampler), with a total volume of air sampled over a 24-hour period being about 25 m^3, extraction of the collected particulate matter with 25 mL of water would yield a $SO_4^=$ concentration in the extract of between 2 and 20 µg/mL, assuming the concentration of the airborne $SO_4^=$ fell in the range of 2 to 20 µg/m^3. Of the methods contained in Table 13, only the Colovos version of the MTB and the IC (0.5 mL sample loop) methods have an adequate working range. Here again, for the determination of atmospheric $SO_4^=$ concentrations, the Colovos-MTB method would be entirely satisfactory. However, if the extracts of smaller air samples were to be analyzed, the IC method would almost certainly have to be used to obtain acceptable accuracy and precision in the results. Another situation requiring the IC method would be the analysis of filter extracts of air samples where the $SO_4^=$ concentration was $\leq$ 1 µg/m^3. Generally, any sampling/extraction procedure which results in solutions containing $\leq$ 3 µg $SO_4^=$/mL would require the use of the IC method.

The results of intermethod comparison studies using real samples of airborne particles collected on filters are summarized in Table 14. A review of Table 14 shows that, generally, the methods compare favourably. The results for the BC/MTB comparison are relatively poor (Sy.x = 4.19), as are the comparisons between the turbidimetric procedures (SV, AIHL 75) and the other methods (Sy.x$\sim$ 3), probably as the result of the greater scatter in the data for the turbidimetric methods with $SO_4^=$ concentrations < 10 µg/mL.

Another procedure for the analysis of filter-collected particles which is gaining popularity is energy dispersive X-ray fluorescence (EDXRF). The advantages of this procedure include sensitivity, accuracy, no sample handling or work up, and results that are in good agreement with those obtained by the extraction/wet chemical procedure, as can be seen from Table 14. The method requires the use of a Teflon or

TABLE 13 SUMMARY OF REPORTED RESULTS FOR DIFFERENT ANALYTICAL METHODS*

Method	Working Range† µg/mL	Accuracy Obs/Exp.	Precision C.V.%††	Operational Mode §	Potential Interferent(s)
Methylthymol Blue (MTB)					
- MRI	17 - 90	1.06	≤5	A	$SiO_3^=$, $PO_4^=$, Clay
- AIHL	7 - 75		≤5.5	A	$SiO_3^=$, $PO_4^=$, Clay
	4 - 75	0.93	≤7		
- Colovos	2 to ≥10	0.98	<5	A	Certain organics, clay
Thorin-Brosset Modified	3 - 14	-	≤3	M	Ca^{++} (?), Clay
Barium Chloranilate	10 - 50	0.99	<6	M	Cl^-, $PO_4^=$
Turbidimetry					
- AIHL No. 61	5 - 70	±10%	∿3	M	Clay, some organics, sulphur anions
- AIHL No. 75	7 - 70	1.04	∿3	M	Clay, some organics, sulphur anions
- SulfaVer IV	9 to ≥70	1.06	≤6	M	Clay, some organics, sulphur anions
AIHL Microchemical	1 to 12.5	0.96	3 (6 - 12.5 µg/mL) 13 (1 - 4.5 mg/mL)	M	Sulphur anions, clay, Ca^{++}
Ion Chromatography (IC)					
- 0.03 mL loop	7 to 111	0.99	<3	A or M	NO_3^- (minor)
- 0.5 mL loop	1 to >20	0.91	<5	A or M	NO_3^- (minor)
- Concentrator Column	<0.1 to >5	<8%		M	NO_3^- (minor)

* Compiled from data in references 66, 67, 68, 69 and 70.

† Accuracy determined by comparing observed results to the nominal values for impregnated EPA audit strips or solutions obtained by dilution of a sample with $SO_4^=$ concentration in the optional range of the method.

†† Co-efficient of variation = $(\sigma/_{mean}) \times 10^2$.

§ A = automatic
M = manual

cellulose filter medium, which precludes the method being used in high volume sampling networks for reasons already discussed (see $SO_4^=$ sampling section). However, the method is ideally suited for samples obtained with low volume, size fractionating (dichotomous) samplers which typically use a Teflon filter for the particle collection. In addition to the study referred to in Table 14, a recent interlab, intermethod comparison study (74) demonstrated that the $SO_4^=$ results obtained by IC and EDXRF were in good agreement.

Although EDXRF offers some attractive advantages, some important caveats about the method should be borne in mind; these relate to the correction factors that must be used to obtain meaningful results. The correction factors must be applied to compensate for X-ray attenuation by the filter medium itself, by the layers of collected particulate matter and by absorption within larger particles ($d > 2\ \mu m$), and for co-incident emissions from other co-collected elements on the filter medium (76).

Thus, it is critical that the standard samples represent, as closely as possible, the real samples with respect to composition, particle size, sample load and filter medium used.

4.2 NO_3^- Analytical Methods

Table 15 summarizes the analytical methods which have been reviewed. Generally, the evaluations of the NO_3^- analytical methods, have not been as exhaustive or numerous as those for $SO_4^=$. This is probably largely the result of the excellent agreement between the popular NO_3^- reduction diazotization procedure (Saltzman (71), Technicon (71)) and ion chromatography that has been found in the studies to date (22, 44, 71, 72, 75).

Also, for the aqueous extracts of air particulate matter, there are no known interferents of any consequence for either method. For example, the analysis of aqueous extracts of particulate matter collected on glass fibre filter by the Technicon method (Technicon method 100-70W) and ion chromatography in the range of 35 to 180 μg NO_3^-/mL yielded a ratio of means by the two methods of 1.00 (22). The maximum difference observed between the two methods was 12%.

In another report (71), the analysis of aqueous extracts of particulate matter collected on Teflon filters in the range of 0 to 3 μg NO_3^-/mL also showed very good agreement between the two methods. The regression equation between the two methods is as follows:

$$NO_3^-\ (\text{Autoanalyzer}) = 0.990\ (NO_3^-\ \text{by IC}) + 0.041$$
$$r = 0.995$$

TABLE 14 STATISTICAL SUMMARY OF INTERMETHOD STUDIES*

Regression Equation	r	Sy.x§	Comments/References
BT = 0.93 (MTB) - 0.61	0.750	0.75	LR for MTB†. Extract from high volume sample (66).
BT = 0.97 (MTB) - 0.49	0.996	0.77	NLR for MTBF††. Extract from low volume sample (66).
BC = 0.92 (MTB) + 0.89	0.999	0.38	LR for MTB. Extract from high volume sample (66).
BC = 0.95 (MTB) - 1.49	0.860	4.19	LR for MTB. Low volume sample extract (66).
EDXRF = 0.73 (BT) + 3.37	0.978	1.35	NLR for MTB. Low volume sample extract (66).
EDXRF = 0.73 (BT) + 3.74	0.981	1.26	NLR for MTB. Low volume sample extract (66).
SV = 1.1 (AIHL 75) - 0.57	0.998	3.00	High volume sample extract (68).
(MRI/MTB) = 1.06 (AIHL 75) - 0.759	0.997	3.43	High volume sample extract (68).
IC = 1.08 (AIHL 75) - 0.022	0.998	2.76	High volume sample extract (68).
(C/MTB) = 1.01 (AIHL 75) + 0.774	0.999	1.72	High volume sample extract (68).
SV = 1.03 (C-MTB) + 5.91	0.997	3.50	High volume sample extract (69).
IC = 0.939 (MTB) - 0.053	0.998	0.157	Low volume sample extract (69).
AIHL Micro = 0.911 •(MTB) + 0.154	0.995	0.236	Low volume sample extract (69).
IC = 0.98 (EDXRF) + 0.04	0.997		Low volume sample extract, fine fraction (36).
IC = 0.92 (EDXRF) - 0.30	0.905		Low volume sample extract, coarse fraction (36).

* Intermethod comparisons performed on aqueous extracts of airborne particulate matter collected with glass fibre (high volume) or Teflon (low volume) filters.
† Linear regression calibration curve used for MTB method.
†† Non-linear regression (3rd order) calibration curve used for MTB method.
§ Standard error of the estimate.

Legend to Table 14

BT = Brosset modified Thorin method (66, 67).
MTB = State of California Air and Industrial Hygiene Laboratories (AIHL) version of methylthymol blue method (66).
AIHL Micro = AIHL colorimetric method for small samples (69, 70).
BC = Barium Chloranilate method (66).
EDXRF = Energy dispersive X-ray fluorescence method (36).
SV = SulfaVer IV Turbidimetric method (68, 69).
AIHL75 = AIHL Turbidimetric method No. 75 (68).
(MRI/MTB) = Midwest Research Institute MTB method (68).
IC = Ion Chromatography (68, 69).
(C/MTB) = Colovos modified MTB method (68, 73).

TABLE 15 SUMMARY OF NO_3^- ANALYTICAL METHODS REVIEWED

Method	References
Reduction-Diazotization - Colorimetric Determination	22, 44, 71, 72, 75, 77
Selective Ionelectrode	44
Ion Chromatography	22, 44, 71, 72, 75

Also, the analysis of artificially prepared standards yielded results which differed by < 5%, even without accounting for errors due to the substantial dilutions involved.

These results agree with the earlier report of Mulik et al. (75), which found excellent agreement between the methods for extracts in the concentration range of 5 to 25 μg NO_3^-/mL of solution.

Based upon these findings, the use of either method can be recommended for the analysis of aqueous extracts of airborne particulate matter with NO_3^- concentrations in the range of 0 to 550 μg/mL.

An evaluation of the ion selective electrode vs. the Technicon method involving 12 extracts showed that the ratio of the means by the two methods was 1.02, r = 0.054 with a maximum observed spread of 16% (44) for the concentration range of 30 to 35 μg NO_3^-/mL. However, for the ion selective electrode, the "standard addition" method was needed to obtain these results. Thus, it appears that for extracts in this concentration range (30 to 550 μg/mL) at least, the ion selective electrode method for NO_3^- yields essentially the same results as the Technicon method.

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